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## Packed Bed Absorption Studies on $N_2O_4$ and MMH

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The Task 2 Statement of Work was concerned with Packed Bed Absorption studies on $N_2O_4$ and MMH. The Statement of Work is delineated below:

"The contractor will conduct experiments with a model packed bed scrubber system to determine the efficiency of vapor phase $NO_2$ absorption using water, caustic solution, ozone, hydrogen peroxide, and various combinations of these in the scrubbing solution. The contractor will also conduct experiments using this model to determine the efficiency of packed bed scrubbing of vapor phase monomethyl hydrazine (MMH) using water and NaOCl scrubbing solutions.

"The experimental apparatus will be constructed as shown on the following page. It will yield data that will allow the contractor to validly extrapolate to conditions at the launch pad, the OPF and HMF facilities at KSC.

"The data obtained will permit the contractor to determine if the use of the aforementioned chemical oxidizing agents can appreciably reduce $NO_2$ and MMH emissions below those levels which can be obtained by packed bed water scrubbing alone. They will be of such quality as to allow the contractor to scale-up and specify design criteria for a full size packed bed scrubber. All the necessary data shall be collected no later than ninety days after the start of Phase 6."

F.I.T. has performed all the above contract requirements, and in addition has investigated the following agents as scrubber liquor additives for $N_2O_4$:

1. Ammonium hydroxide, $NH_4OH$
2. Triethanolamine, $N(CH_2CH_2OH)_3$
3. Sodium sulfite, $Na_2SO_3$
4. Sodium hypochlorite, NaOCl
5. Urea, $H_2N-\overset{O}{\overset{\|}{C}}-NH_2$
6. Ferrous sulfate, $FeSO_4$
7. Freon
8. Sodium Carbonate, $Na_2CO_3$

Also, contract amendments which allowed sub-contracting work to Martin Marietta Corporation (MMC) were negotiated. These sub-contracts involved scrubber construction and scale-up experiments concerning the caustic solution (NaOH) system for $N_2O_4$ absorption and the hypochlorite (NaOCl) absorption system for MMH.

The conclusions stated in this report are tentative and subject to change or correction pending completion of the work still being performed at FIT. The changes will appear in the final report.

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# INTRODUCTION

## 1. FUNDAMENTAL CHEMISTRY OF $N_2O_4$ ABSORPTION

The $NO_x$ wet scrubbing absorption process has been studied extensively for decades, but much of the physical and chemical phenomena are still little understood. Radian Corporation, in their 1971 two-volume $NO_x$ absorption treatise, states:[1]

"The fact remains that an adequate theoretical description of the process has not been given. It is not known under what conditions gas or liquid film diffusion limits the rate of aqueous absorption. Further, the mechanism and kinetics of the reaction between water and nitrogen oxides have not yet been established."

Andrew and Hanson in their "Dynamics of Nitrous Gas Absorption", considered ten different mechanisms by which nitrogen oxides might be absorbed.[2]

However, certain general fundamentals have been ascertained over the years:

1. $NO_2$, the monomer, is completely insoluble, as contrasted to $N_2O_4$, the dimer, which is somewhat soluble.
2. $HNO_2$ must be immediately destroyed or must be prevented from forming in order to increase absorption.
3. The NO, $NO_2$ ratio should be 1:1 to effect maximum solubility

These fundamentals are explained by the following data. The standard textbook equation used to describe the solubilization of $NO_2$ is:

$$3NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$$
$$3HNO_2 \longrightarrow HNO_3 + H_2O + 2NO$$

If $NO_2$ were soluble, it should be scrubbed easily. Researchers have also found that the rate of its absorption into water is proportional to the square of its concentration. This leads inevitably to the conclusion that it is the dimer $N_2O_4$ which is being absorbed. Thus the intensity of brown color is a sign of insolu-

Nearly all researchers are in agreement that a 1:1 ratio of NO to $NO_2$ is ideal, both for speed and completeness of absorption, in both plain water and in alkali solution. Apparently this is so because the $N_2O_3$ ($NO + NO_2$) molecule is absorbed faster than $N_2O_4$.[3,4] Spectroscopic analysis has indicated that the following reactions are taking place:[5]

1. $$N_2O_4 \longrightarrow NO^{\oplus} + NO_3^{\ominus} \xrightarrow{H_2O} HONOH^{\oplus} + NO_3^{\ominus} \longrightarrow 2H^{\oplus} + NO_2^{\ominus} + NO_3^{\ominus}$$

2. $$N_2O_3 \longrightarrow NO^{\oplus} + NO_2^{\ominus} \xrightarrow{H_2O} HONOH^{\oplus} + NO_2^{\ominus} \longrightarrow 2H^{\oplus} + 2NO_2^{\ominus}$$

However, these equations cannot really explain the difference in the solubilities between $N_2O_3$ and $N_2O_4$, and it is thought that $N_2O_4$ absorption equations may even be more complex than that described above.[6,7] Most researchers have found that pure water shows higher rates of absorption of $NO_x$ on one pass than caustic solutions, the rate decreasing with increasing alkalinity.[8,9,10] Perelman and Kantoravich[11] explained this lower absorption rate by postulating that the liquid film resistance is rate controlling and this resistance increased with alkalinity. If this is true, systems which minimize surface tension should reduce resistance to a minimum. Another postulated reason why non-recirculated water is more efficient than alkali solutions is the tendency of alkaline nitrites to be oxidized by $NO_2$ to nitrate yielding NO.[12]

$$Ca(NO_2)_2 + 2NO_2 \rightleftharpoons Ca(NO_3)_2 + 2NO$$

This is why some workers have found nitrates forming when only $N_2O_3$ is being absorbed since with this gas alone, one should expect only nitrites.[13]

$$2Ca(OH)_2 + N_2O_3 \longrightarrow 2Ca(NO_2)_2$$

The rate equations which seems to describe the absorption process for $NO_x$ in water are:[14]

$$\frac{-d(NO_2)g}{dt} = K(NO_2)_g^2 + K^1(NO)_g(NO_2)_g - K^{11}(HNO_2)^2$$

$$\frac{-d(NO)_g}{dt} = K^1 (NO)\ (NO_2)_g - K^{11}\ (HNO_2)_l^2$$

Thus the inhibiting effect of absorption of both $NO_2$ is inversely proportional to the square of the nitrous acid concentration. Also according to these equations the greatest absorption rate is obtained when the NO concentration is equal to the $NO_2$ concentration (so as to perhaps form soluble $N_2O_3$). Other research has indicated an even faster dissociation of $HNO_2$. If one combines reaction one and two below equation three results:[15,16]

1. $4HNO_2 \rightleftharpoons N_2O_4 + 2NO + 2H_2O$
2. $N_2O_4 + H_2O \rightleftharpoons HNO_2 + HNO_3$
3. $3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O$

The expression for nitrous acid decomposition (equation 1) rate is described below:

$$\frac{dHNO_2}{dt} = \frac{(HNO_2)^4}{(N_2O_4)\ (NO)^2\ (H_2O)^2}$$

Thus the rate of decomposition of nitrous acid is proportional to the fourth power of its concentration. However, this equation is not the rate limiting step. The rate limiting step is described by equation 3 which is much slower.

If an absorbing water solution is recirculated without additive, the buildup of hydrogen ions together with nitrate and small quantity of nitrite ions, theoretically would prevent effective scrubbing. Nitrates and nitrites formed when an alkaline additive is present are also rate inhibiting, with the nitrites causing a greater reduction in efficiency,[17,18] probably due to the effect on the decomposition of $HNO_2$.

## 2. REPORTED EFFECTIVE SCRUBBING AGENTS FOR $N_2O_4$

a. Concentrated Sulfuric Acid, $H_2SO_4$.

Concentrated Sulfuric Acid has been reported as a good absorber of $NO_x$ when the $NO/NO_2$ mixture is in a 50:50 ratio.[19]

b. 20-35% Nitric Acid, $HNO_3$.

This concentration of nitric acid has been reported as a good absorber of $N_2O_3$ ($NO/NO_2$, 1:1)[19]

c. Calcium Oxide, CaO.

~~Sine~~ Since any practical NO scrubber process would need recirculated water, an alkali additive is necessary. Since high pH can inhibit absorption, CaO as an additive may be better than NaOH or KOH. CaO is only slightly soluble in water, but will form the hydroxide "as needed" when the scrubber water takes on acid. Thus using this method the pH does not rise very high. Also the basic salt $Ca(OH)_2 \cdot Ca(NO_2)_2 \cdot 2H_2O$ forms.[20]

d. Magnesium Hydroxide, $Mg(OH)_2$.[21]

Same reasoning as for CaO.

e. Ammonium Sulphite, $(NH_4)_2\ SO_3$ [22]

Esso has reported that the sulphite ion shows a remarkable capacity to absorb $NO_2$. It does this in a wide range of pH and at temperatures of 125°F (where little $N_2O_4$ exists). Efficiencies were almost always 100%. Although the chemistry of the reaction is not completely known, the classical $NO_2$ absorption equation does not apply, since NO is not given off.

f. Ammonium Ion, $NH_4^{\oplus}$. The ammonium ion was shown to be an absorber for NO. The results were not as impressive as with sulphite ion and lower temperatures improved efficiency.[23]

g. Potassium Permanganate, $KMnO_4$.

The caustic permanganate reaction is thought to be:

$$2NaOH + 2KMnO_4 + 2NO_2 \longrightarrow K_2MnO_4 + Na_2MnO_4 + 2HNO_3$$

The nitric acid formed is neutralized by excess caustic. The permanganate reaction for NO is:

$$NO + KMnO_4 \longrightarrow KMnO_3 + MnO_2\downarrow \quad ^{24}$$

h. Urea, $H_2N-\overset{\overset{O}{\|}}{C}-NH_2$

Urea reacts with nitrous acid in the following manner:

$$H_2N-\overset{\overset{O}{\|}}{C}-NH_2 + HNO_2 \longrightarrow CO_2 + N_2 + H_2O$$

Urea has no effect on the concentration of $HNO_3$. It has long been used as an additive in strong nitric acid solutions to prevent release of $NO_x$. This method is common in the metal pickling industry and in phosphate rock acidulation.[25,26]

i. Ferrous Salts, Fe++

$FeCl_2$ and $FeSO_4$ form a FeNO++ complex which may be reversed to release the NO. NO scrubbing rate seems to be unaffected by the concentration of ferrous ions. Apparently the rate of removal is also not sensitive to gas velocity in the range tested 7 to 100 cm/sec, through a packed bed type scrubber.[27,28,29]

j. $NH_4OH$, $NH_4NO_3$ [23]

k. $NH_4OH$ [23]

l. Aliphatic and aromatic amines [30]

m. Ethanolamine [31]

n. $NH_4Cl$

o. $NH_4OAc$

p. $NaClO_2$ [32]

q. NaOCl

r. $Na_2SO_3$ [28,33,34]

s. $O_3$ [42]

t. $H_2O_2$ [43]

## 3. EFFECTS OF TEMPERATURE, PRESSURE, AND HUMIDITY ON $N_2O_4$ ABSORPTION

High pressure favors every reaction of $NO_x$ absorption. This is especially the case where the $NO_x$ is raised to a power as shown in the following:

$$K = \frac{(HNO_3)^2 \ (NO)}{(NO_2)^3 \ (H_2O)}$$

$$K = \frac{(NaNO_2) \ (NaNO_3) \ (H_2O)}{(NO_2)^2 \ (NaOH)^2}$$

The following illustrates some of the effects of temperature on key equilibrium expression of $NO_2$ absorption:

$$K_p = \frac{(NO_2)^2}{(NO)^2(O_2)}$$

| $T^oF$ | $K_p$ [35] |
|---|---|
| 35 | $9.4 \times 10^6$ |
| 80 | $1.19 \times 10^6$ |
| 170 | $4.61 \times 10^4$ |

$$K_p = \frac{N_2O_3}{(NO) \ (NO_2)}$$

| $T^oF$ | $K_p$ [36] |
|---|---|
| 25 | 0.475 |
| 35 | 0.272 |
| 45 | 0.145 |

$$K_p = \frac{(N_2O_4)^2}{(NO_2)^2}$$

| $T^oF$ | $K_p$ [37] |
|---|---|
| 0 | 65 |
| 20 | 12 |
| 40 | 2.7 |
| 60 | 0.67 |
| 80 | 0.20 |

$$K_p = \frac{(HNO_2)^2}{(NO) \ (NO_2) \ (H_2O)}$$

| $T^oF$ | $K_p$ [38] |
|---|---|
| 20 | 1.56 |
| 40 | 0.64 |
| 60.5 | 0.25 |
| 80.6 | 0.11 |

$$K = \frac{(HNO_3)^2 (NO)}{(NO_2)^3 (H_2O)}$$

| $T^oF$ | $K_p$ [39] |
|---|---|
| 2 | $3.78 \times 10^{-3}$ |
| 27 | $9.51 \times 10^{-3}$ |
| 77 | $1.01 \times 10^{-3}$ |
| 127 | $1.87 \times 10^{-3}$ |

$NO_x$ can exist as NO, $NO_2$, $N_2O_4$, $N_2O_3$, $HNO_2$, and $HNO_3$. Under dry conditions, the equilibrium is nearly all to the left, favoring NO and $NO_2$, the least soluble species. Heat and humidity shift the equilibrium to the right. As an example, starting with a 1:1 ratio of NO to $NO_2$ at a total of 5000 ppm, with 8000 ppm $H_2O$, at room temperature at 1 atm. pressure, the relative mole fractions would be:[40]

| NO | $NO_2$ | $N_2O_4$ | $N_2O_3$ | $HNO_2$ | $HNO_3$ |
|---|---|---|---|---|---|
| $2.4 \times 10^{-3}$ | $2.4 \times 10^{-3}$ | $3.9 \times 10^{-6}$ | $5.3 \times 10^{-7}$ | $1.7 \times 10^{-4}$ | $2.7 \times 10^{-5}$ |

According to one source, the nitrous acid formed is proportional to the square of the water vapor pressure.[41]

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# CHAPTER 1

## EXPERIMENTS USING WATER, CAUSTIC SOLUTION (NaOH), OZONE ($O_3$), AND HYDROGEN PEROXIDE ($H_2O_2$) AS SCRUBBING AGENTS FOR $N_2O_4$.

## 1. BASIC PRINCIPLES AND PARAMETERS OF THE EXPERIMENTAL SCRUBBING APPARATUS

The calculations on the capacities of gas absorption columns are based on simple material balances and on rates of absorption. Absorption columns are almost universally operated on the counter current flow principle. Where a small volume of absorption liquor must be used, the liquor may be continuously recirculated in the tower in order to adequately wet the surfaces of the column packing.

An increase in mass velocity of the gas stream reduces the diameter of bed required, but this advantage is rapidly off-set by the increased pressure drops through the bed and the increased power requirement for the blowers (if used). If the mass velocity is reduced excessively to minimize pressure drop the required diameter of the bed becomes so large as to introduce channeling and back mixing. As the mass velocity is decreased, it is preferable to have more than one scrubber to avoid these defects.

The usual ratio of column height to diameter is from 3 to 10 to 1. The higher the column the longer the detention time, the higher the percentage absorption efficiency. The diameter affects the capacity not the efficiency. In other words, height of the column increases efficiency, diameter of column gives capacity.

Increase in operating pressure of the scrubber would increase the absorption efficiency and or decrease the required size of the scrubber. However, it is believed that the compression costs would add to the operating cost greatly and only increase the efficiency slightly due to the high dilution. Further, the very low and variable feed rate from the venting would preclude use of a compressor in the first place.

The working conditions for the wet scrubber at this time may be summarized as follows:

Temperature of Feed Gas, ambient to 35$^{o}$C

Temperature of Scrub Liquor, ambient to 35$^{o}$C

Adiabatic operation of scrubber

$\Delta$ P, atmospheric to atmospheric plus 10 inches of $H_2O$

Liquid recirculation, 20 GPM minimum

Thickness of packing bed, 7 feet, Diameter of Scrubber, 2 feet

Gas Flow, 0 - 400 SCFM

In order to determine the optimum wet scrubbing liquors and conditions, a small scale experimental apparatus described in Figure 6, page was assembled at F.I.T. This apparatus was used to conduct the following experiments.

## 2. WATER SCRUBBING OF $N_2O_4$

Several plain water runs were made to study the reproducibility of the scrubbing operation and to provide background data for comparing the efficacy of the additives in the scrubber liquor.

The results of five series of runs made with plain water are shown in Table 1. The scrubber absorption efficiencies range from 88.9% to 95.9%. The average efficiency for each pass is also shown. An overall average efficiency for these five runs was 93.5%. This is one of the figures used for comparing the results of the runs made with additives. Reproducibility from run to run, through not perfect, was considered adequate for the system.

Analysis of the gaseous effluent from the column shows a minimum of 340 ppm to a maximum of 3400 ppm $NO_x$ depending on various factors such as inlet gas $NO_x$ concentration, number of passes as well as other variables.

These data also show, as was expected, that as the scrubber liquor is recycled, the efficiency of scrubbing decreases rapidly resulting in increased concentration of $NO_x$ in the exit gas. For example, in Run 1, efficiency drops from 95.9 in the first pass to 93.9% in the third pass, while the $NO_x$ concentration increases from 1170 to 1750 ppm.

Further, efficiency is somewhat dependent on inlet gas concentration. In Run 2 and Run 5 (fourth pass) when the inlet $NO_x$ concentration was in the 8-9000 ppm range, efficiency dropped below 90%. This indicates that scrubber efficiency drops with a decrease in $NO_x$ concentration - a significant factor in operating a system with a variable feed rate.

The $NO_3$ concentration in scrubber liquor is seen to increase as each pass is executed. Consequently, as the $HNO_3/HNO_2$ content builds up and the vapor pressure of the solute increases in the liquor, the exit gas becomes richer in $NO_x$. A 3,000 ppm solution is approximately 0.3% in $HNO_3/HNO_2$ concentration. This amount of

solute exerts a significant vapor pressure as is shown in Figure 38, page 113, Phase III, Final Report. The partial pressure of $HNO_3/H_2O$ mixtures at small mole fractions is several mm Hg which is sufficient to yield unacceptable $NO_x$ emissions.

The amount of $NO_3/NO_2$ formed in the scrubber liquor is seen to increase rapidly to several thousand ppm as recycling continues. The off gas $NO_x$ concentration increases linearly as the recycling progresses.

It is evident from these results that a plain water recycling scrubbing system is not suitable for absorbing $NO_x$ vapor in gas stream to the low levels acceptable for Shuttle pad servicing operations.

Separate dry gas analysis of NO and $NO_2$ would have been desirable but was not performed due to unavailability of a Teledyne instrument. Instead, the wet chemical method, which is quite laborious was used giving the combined NO and $NO_2$ concnetration and expressed as $NO_x$ in the tables of results.

A series of runs were conducted to illustrate the effect of water flow on the efficiency of absorption. The results are shown in Figures 1, 2, and 3. As is seen greater efficiency of $N_2O_4$ scrubbing is obtained with higher water flow rates. The "outlet" figures refer to those concentrations of $NO_2$ in the effluent from a second stage "dry" scrubber which will be discussed in other sections of this report. The "mid" concentrations are in the effluent for the wet scrubber

TABLE 1

SUMMARY OF RUNS ($N_2O_4$ and $H_2O$)

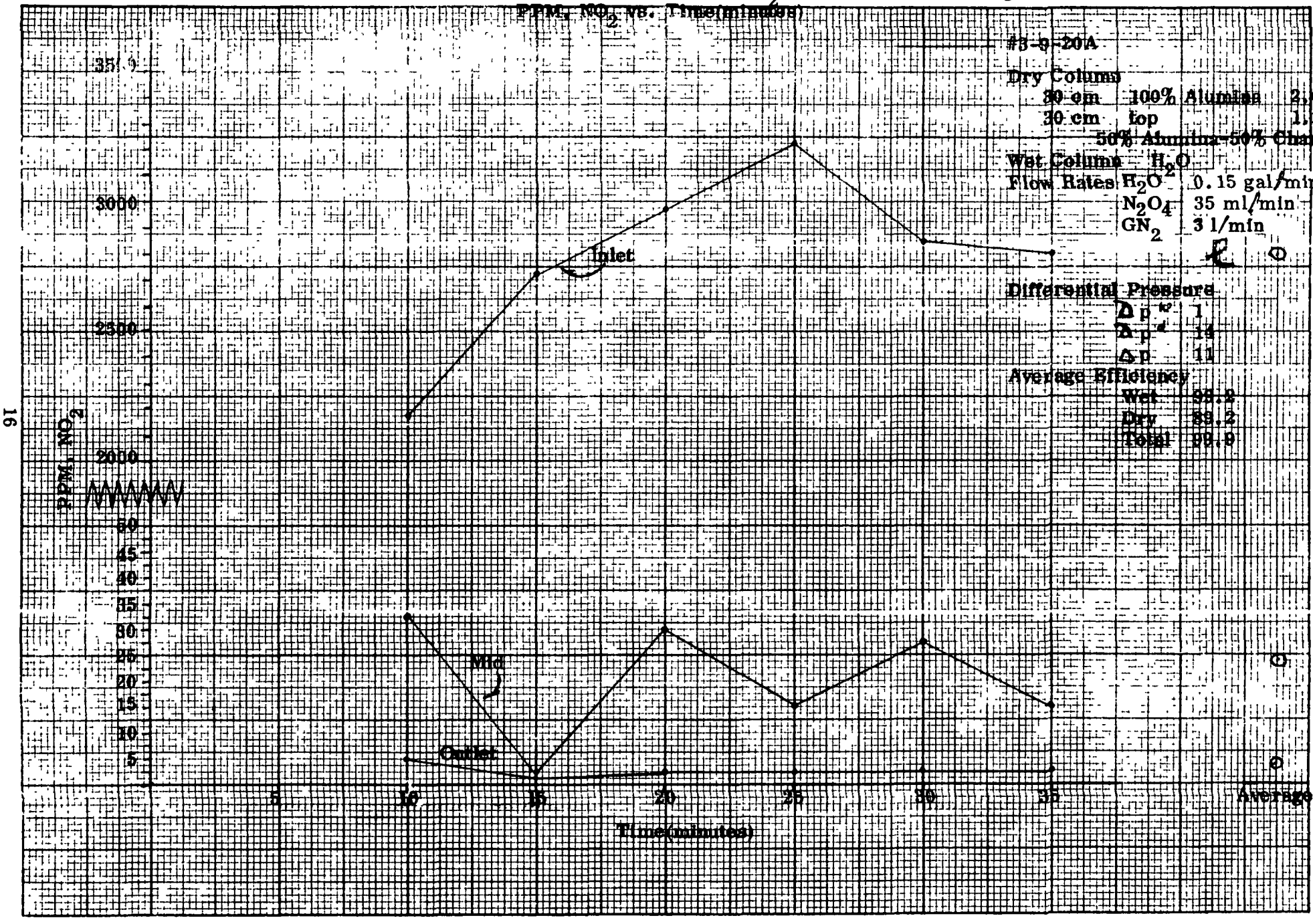
| | Date | Oxidant | Scrubber liquor Composition | Inlet Gas Concentration ppm NOx | Off Gas Concentration ppm NOx | $NO_3$ Residual in Scrubber Liquor, ppm | Pass Number | % Absorption Efficiency |
|---|---|---|---|---|---|---|---|---|
| | 3/25 | None | Plain $H_2O$ | 28,800 | 1,170 | 400 | 1st | 95.9 |
| (1) | 3/25 | None | " | " | 1,480 | 1,584 | 2nd | 94.7 |
| | 3/25 | " | " | " | 1,750 | 3,124 | 3rd | 93.9 |
| | | | | | | | Run Avg. | 94.8% |
| (2) | 3/24 | " | " | 7,770 | 863 | n/a | 1st | 88.9 |
| (3) | 4/12 | " | " | 36,000 | 2,570 | - | 1st | 92.8 |
| | 4/12 | " | " | 19.400 | 1,085 | - | 2nd | 94.4 |
| | 4/13 | " | " | 7,500 | 480 | - | 3rd | 93.6 |
| | | | | | | | Run Avg. | 93.6% |
| (4) | 4/13 (flooded tower) | " | " | 46,000 | 3,400 | - | 1st | 92.6 |
| (5) | 4/29 | " | " | 8,550 | 340 | 1,190 | 1st | 95.9 |
| | 4/29 | " | " | 18,250 | 1,020 | 1,760 | 2nd | 94.4 |
| | 4/30 | " | " | 16,800 | 1,170 | 2,750 | 3rd | 93.0 |
| | | | | | | | Run Avg. | 92.3% |

Avg. overall efficiency of 5 runs 93.5%

TOTAL FLOW RATE ($N_2$ + $N_2O_4$) = 3 liters/min (all runs)

PROGRESS 20 X 20 TO THE INCH Z-2282
7 X 10 INCHES

Combination Wet-Dry Scrubber System Utilizing $H_2O$ at Flow Rate of 0.15 gal/min

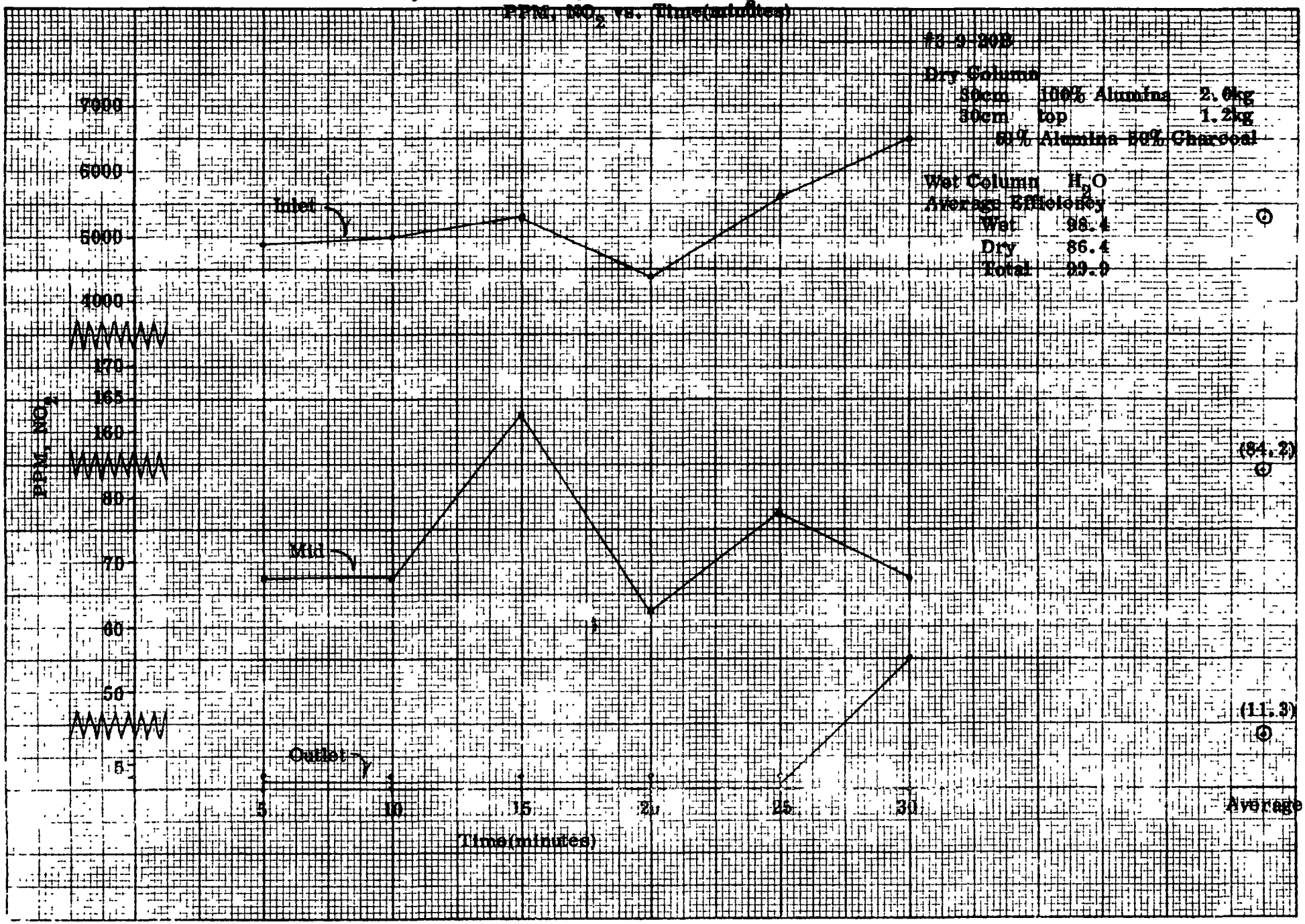





11/5/76 BC

Figure 1

PROGRESS 20 X 20 TO THE INCH 7 X 10 INCHES Z-2282

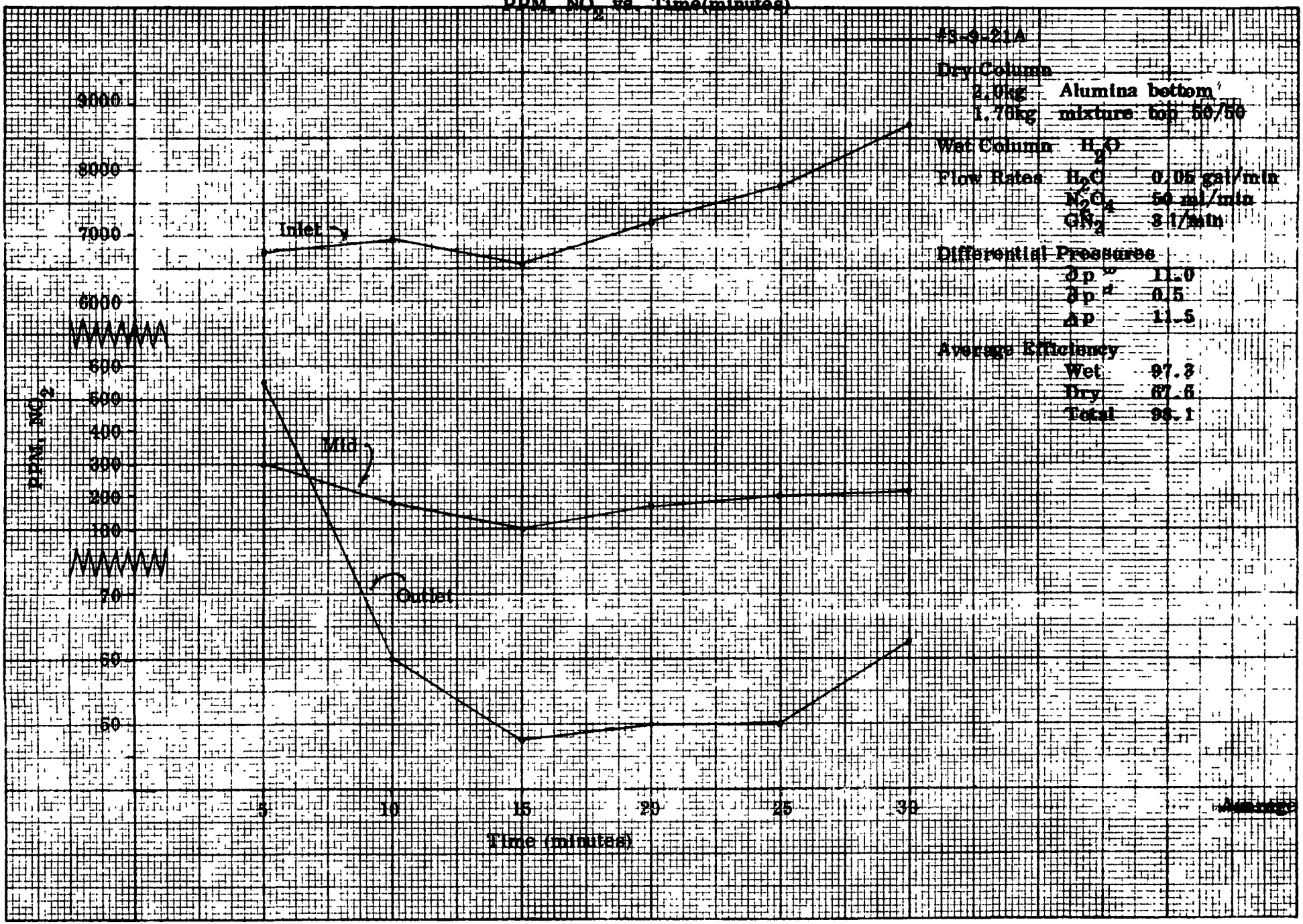



11/5/76

Figure 2

PROGRESS 20 X 20 TO THE INCH Z-2282
7 X 10 INCHES

Combination Wet-Dry Scrubber System Utilizing $H_2O$ at Flow Rate of 0.05 gal/min




11/5/76 BC

Figure 3

## 3. CONCLUSIONS

Plain water is efficient in scrubbing $N_2O_4$ vapors. However, the final effluents certainly do not meet our goals of 10 ppm.

## 4. DISCUSSION OF WET SCRUBBING OF $N_2O_4$ VAPORS USING CAUSTIC SOLUTION BATH

Preliminary test runs showed that use of a NaOH solution in lieu of plain water for scrubbing $N_2O_4$ vapors resulted in considerably higher absorption efficiencies and lower concentrations of NOx in the gaseous effluent. Further, recycling of a fairly weak NaOH solutions (0.1 normal or 0.4%) resulted in fairly rapid exhaustion of the effectiveness of the scrubber liquor necessitating the use of a large volume of scrubber liquor per run. It was deemed adviseable, therefore, to perform test runs with more concentrated baths with further purpose of reducing scrubber liquor volume to a minimum.

A series of test runs was made in the existing wet scrubber using alkaline baths instead of water, with the following results.

A run was made with a 5% NaOH recycled scrubber bath. The results appear in Table 2 as run No. 1a through 1e. Absorption efficiencies were consistently 99.6 to 99.7% with NOx concentration in the gaseous effluents ranging from 30 to 48 ppm, compared to an overall efficiency of 93.5% in $H_2O$ runs and a gaseous effluent containing a few thousand ppm NOx as appear in Table 1.

In Run 2, $\frac{1}{2}$" quartz rounded pebbles were substituted for the $\frac{1}{4}$" Raschig ring packing. Absorption efficiency dropped slightly to 99.3% with off gas above 100 ppm NOx. This drop was attributed to the decreased surface area of quartz pebbles compared to the larger surface area provided by the Raschig rings.

In order to optimize the concentration of NaOH in the scrubbing liquor, a 5- run series was made using 2,4,6,8, and 10% NaOH solutions. The results appear as run nos. 3 through 7 in Table 2. At the 2, 4, and 6% contained NaOH the efficiencies are above 99.7% with off gas NOx 33 ppm or less. However, at 8 or 10% contained NaOH, the efficiency dropped slightly below 99.7%. These

results indicate an optimum NaOH concentration to be in the 2-6% range for maximum efficiency for possible use in the KSC scrubber design. Further, a possible inhibitory effect is noted due to the greater salt content of the 8 to 10% baths. From the practical standpoint a 2 to 6% NaOH concentration is reasonable and will be specified for the full flow evaluation studies at Martin Marietta.

Another series of runs was made with 5% NaOH scrubber liquor with simultaneous introduction of varying amounts of $O_2$ into the pregnant gas. These results appear as runs 8a through 8d. Based on these results it is evident that introduction of $O_2$ into the scrubber up to 10 or 20% did not materially affect the absorption efficiency. There was only a very slight increase, 0.1% in efficiency in a 50% $O_2$ to 50% $N_2$ mixture. It was concluded that addition of $O_2$ into the scrubber provides too small an increase in efficiency to be considered useful for $NO_x$ scrubbing under the operating conditions in these runs.

Run 9 was made in a 2.5% $NH_4OH$ solution in lieu of NaOH. The absorption efficiency was from 99.6 to 98.8% with an off gas from 31 to 130 ppm $NO_x$. Further, the exit gas was cloudy due to formation of an aerosol of $NH_4NO_3$ with a strong $NH_3$ odor resulting from the high volatility of $NH_3$ in the scrubber liquor. Both the odor and the aerosol formation are objectionable. For these reasons $NH_4OH$ in scrubbing liquor is not considered a satisfactory substitute for NaOH without a second stage scrubber.

Based on the above results, the following conclusions were drawn:

1. With the use of certain alkaline baths, the absorption efficiency for wet scrubbing $N_2O_4$ vapors can be increased from 93.5% (plain water) to the 99.7% level. However, these results must be interpreted liberally since plain water efficiency is evidently more dependent upon actual water contact and flow than the other systems. (Figures 4 and 5)

2. Raschig rings by providing a larger surface area are more effective than rounded quartz pebbles as column packing.

3. Moderate strength solutions for NaOH (2 to 6%) are approximately as effective as a weak (0.4%) solution of NaOH in obtaining high absorption efficiency but have the added advantage of a longer life in use.

4. The absorption efficiency starts decreasing in 8 to 10% NaOH scrubber solutions.

5. Use of the 4% NaOH scrubber solution will permit use of a storage tank about 1/10 as small in size as required for a 0.4% solution, i.e. 400 gallons vs. 3500 gas in size.

6. Addition of $O_2$ to the scrubber increases absorption efficiency too slightly to warrant its use.

7. Use of an ammoniacal scrubber liquor gives a relatively high absorption efficiency but releases an odor and an aerosol necessitating a second stage for safe operation.

TABLE 2

Results of Wet Scrubbing $N_2O_4$ Vapors in an Alkaline Bath

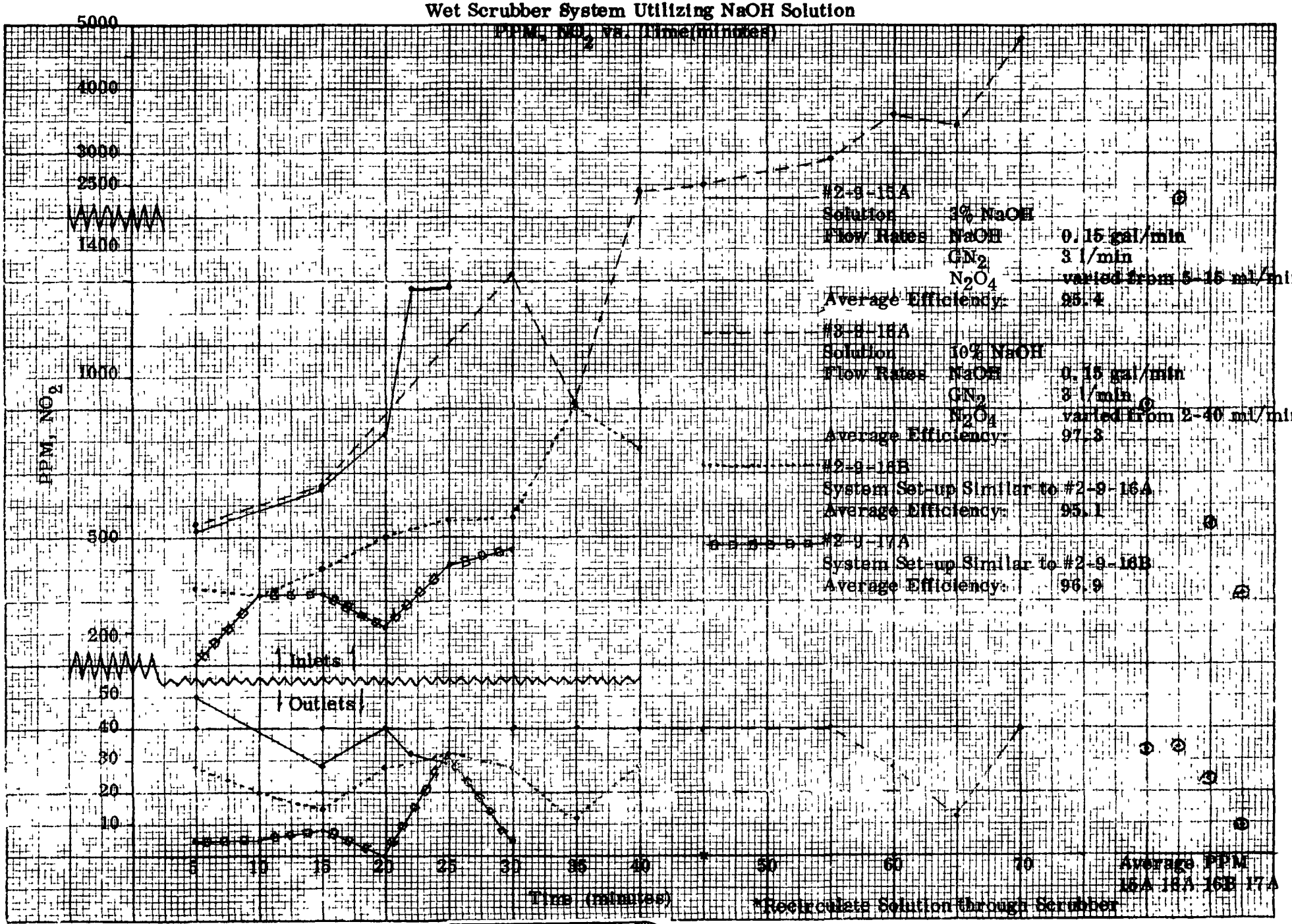
| Run No. | Concen. NaOH in Scrub. Liquor, % | Inlet Gas ppm NOx | Off Gas ppm NOx | Pass No. | Abs. Eff. % | Comments |
|---|---|---|---|---|---|---|
| 1a | 5 | 11,900 | 35 | 1 | 99.70 | |
| 1b | 5 | 14,000 | 48 | 2 | 99.65 | |
| 1c | 5 | 12,500 | 44 | 3 | 99.64 | |
| 1d | 5 | 7,500 | 30 | 4 | 99.60 | |
| 1e | 5 | 11,000 | 44 | 5 | 99.60 | |
| 2 | 10 | 17,100 | 117 | 2 | 99.3 | |
| 3 | 2 | 12,150 | 26 | 1 | 99.78 | |
| 4 | 4 | 12,500 | 33 | 1 | 99.73 | |
| 5 | 6 | 7,000 | 14 | 1 | 99.80 | |
| 6 | 8 | 6,000 | 19 | 1 | 99.68 | |
| 7 | 10 | 7,620 | 36 | 3 | 99.52 | |
| 8a | 5 | 11,000 | 30 | 1 | 99.72 | 5% $O_2$ in $N_2$ |
| 8b | 5 | 11,250 | 33 | 2 | 99.70 | 10% $O_2$ in $N_2$ |
| 8c | 5 | 11,000 | 30 | 3 | 99.72 | 20% $O_2$ in $N_2$ |
| 8d | 5 | 13,200 | 24 | 4 | 99.81 | 50% $O_2$ in $N_2$-slight improvement in eff. |
| 9 | 2.5% $NH_4OH$ * | 11,000 | 31-130 | 1 | 99.6 | Aerosol forms & odor of $NH_3$ is strong in gaseous effluent. |

Total Flow rate ($N_2$ + $N_2O_4$) = 3 liters/min. (all runs)

* To further evaluate $NH_4OH$ as a potential additive to scrubber liquor, additional runs were made using a second stage dry scrubber. The results appear in Chapter 4.

PROGRESS 20 X 20 TO THE INCH 7 X 10 INCHES Z-2282

## Wet Scrubber System Utilizing NaOH Solution




11/5/76 BC

Figure 4

Reproduced from best available copy.

PROGRESS 20 X 20 TO THE INCH 7 X 10 INCHES Z-2282

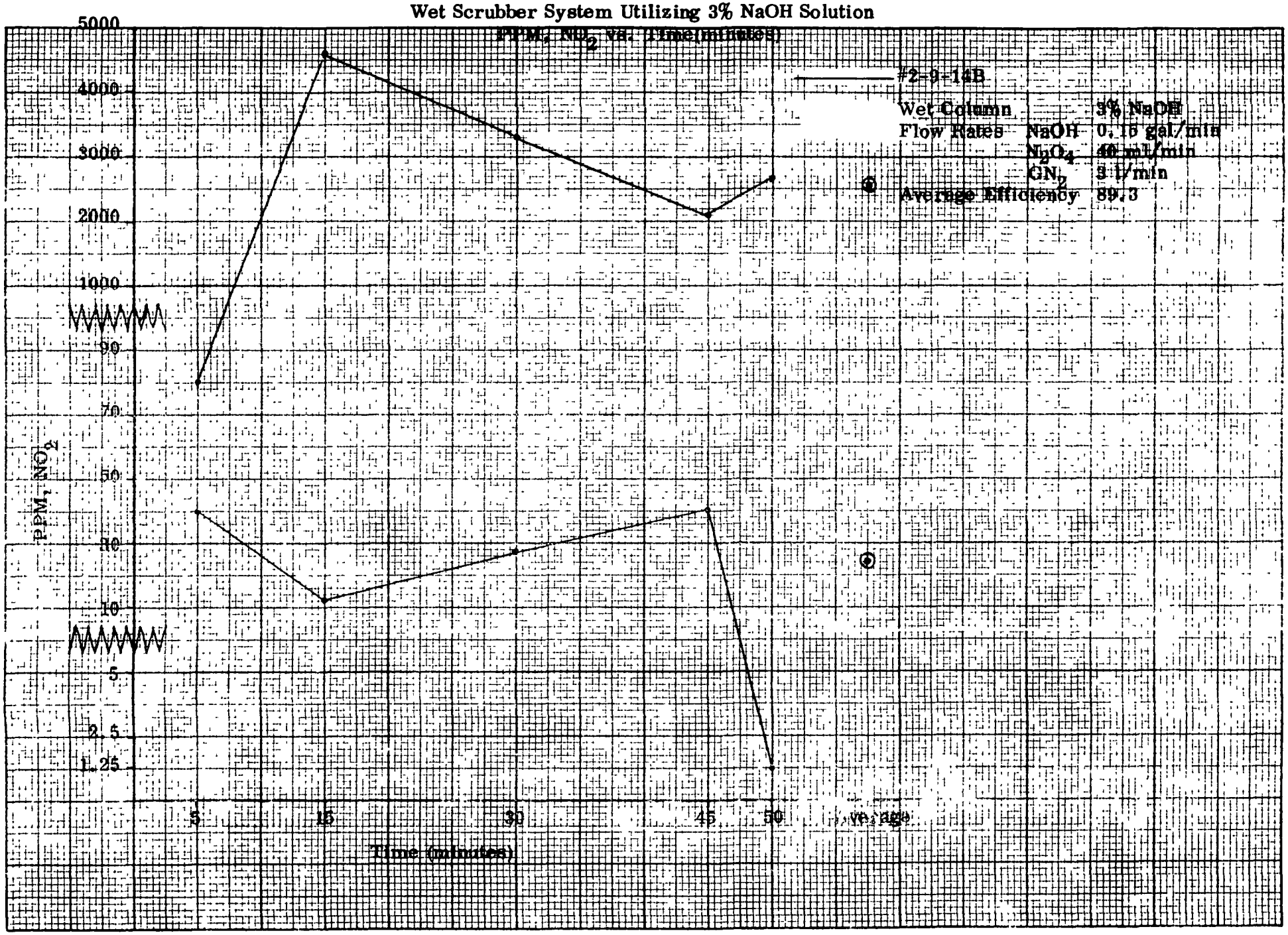



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Figure 5

## 5. COMMENTS ON OZONATED RUNS

Figure 6 shows schematically the wet scrubber system with provision for introducing a gaseous oxidant ($O_3$ and/or $O_2$) upstream of the column. The purpose of the oxidant is to oxidize NO (present in the feed stream mostly as a result of reaction of $NO_2$ with $H_2O$) to the more water soluble $NO_2$ form so as to enhance its capture in the column.

The results of the runs are in Table 3. Run 1 was performed with plain water in a colum 3/4 flooded to partially simulate a bubble cap system. The resulting absorption efficiency averaged about 96%. This was better than plain water without oxidant, as shown in Table 3, where 93.5% was the average of several runs. The off gas $NO_x$ concentration was 70 ppm in the first pass and 83 ppm in the second pass.

Run 2 was made with plain water but the column was not flooded, gave a 99.1% efficiency and an off gas concentration of 67 ppm in spite of a three-fold increase in $NO_2$ in the feed gas.

In Run 3 the flooded column condition was repeated but in an 0.1 normal alkaline bath in lieu of plain water. The absorption efficiency was improved to approximately 98.7% and off gas only in the 20-30 ppm range.

Run 4 was performed with only $O_2$ as oxidant (no $O_3$), a flooded tower and an alkaline bath. The efficiency was 99% with 33 ppm $NO_x$ in the off gas.

Based on the results of these four runs, it was concluded that:

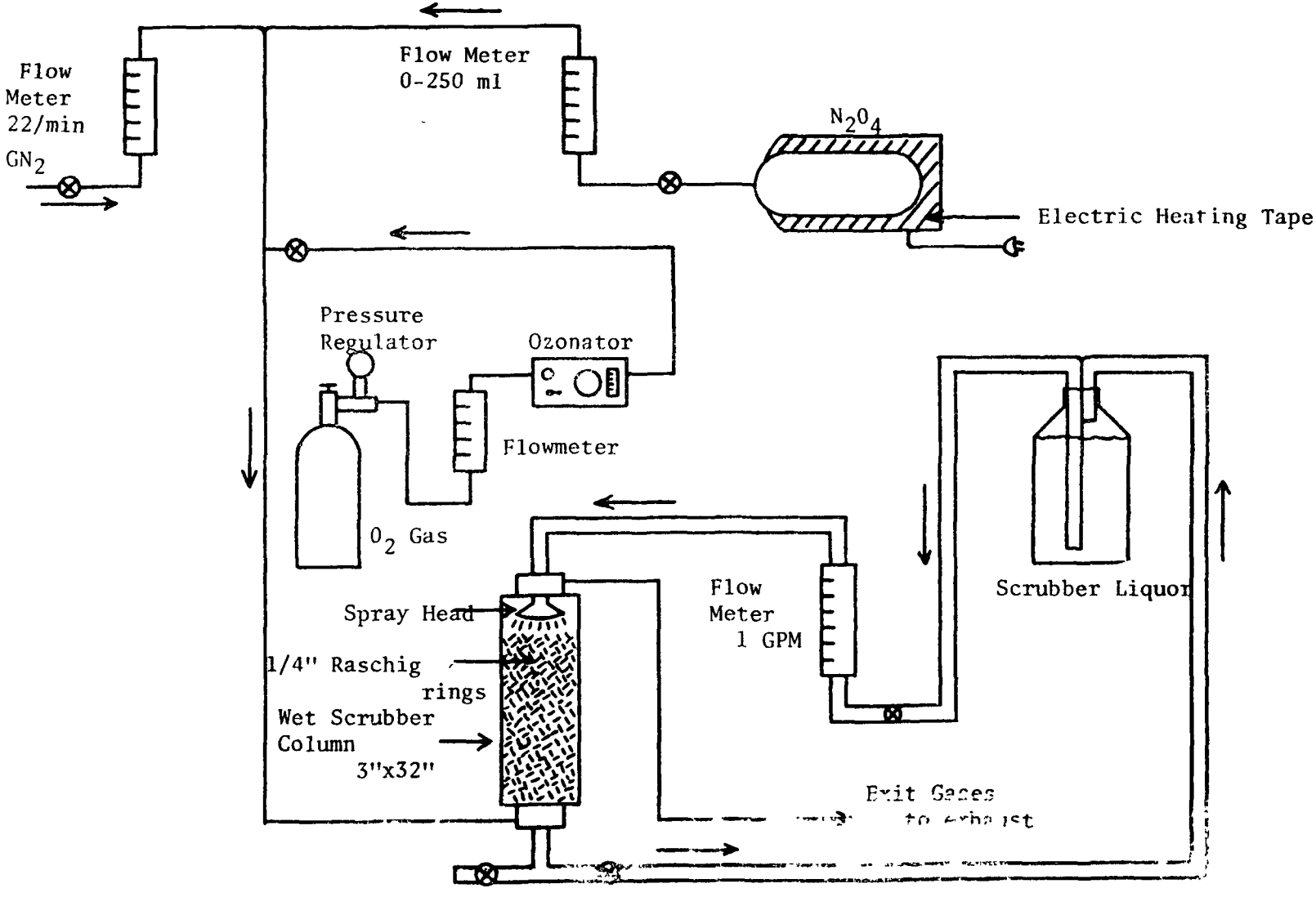
1. Operating with the oxidant in the feed gas slightly increased the absorption of $NO_x$ in the wet scrubbing system.

2. Scrubbing efficiency is increased about 2.5% by operating with an oxidant over the plain $H_2O$ system even in a flooded tower condition.

3. Use of a flooded tower does not provide an optimum condition of operation.

4. The absorption of $NO_x$ is low in the above systems and results in off gas effluents below 100 ppm $NO_x$ but which are still above the 5 ppm requirement.

5. The increase in absorption efficiency is attributed to a partial oxidation of NO to $NO_2$ which is absorbable in $H_2O$ and more absorbable in an alkaline solution




SCHEMATIC SHOWING THE LABORATORY WET SCRUBBER (SET UP #1)

Figure 6

Run 5 performed with plain $H_2O$ and $O_2$, as oxidant, showed an absorption efficiency of 98.64% and 118 ppm $NO_x$ in the gas effluent. In Run 6, with an alkaline bath the absorption efficiency was 99.75% and 27 ppm $NO_x$ in the gas effluent.

Operating conditions in Runs 7a and b were similar to Run 6 except the concentration of $NO_x$ in the inlet gas as well as the gas volume ratio were reduced. The efficiency was 99.43 and 99.26%, respectively, on the thrid and fourth pass with 38 or 39 ppm $NO_x$ gas effluent.

In Runs 8a and b, performed with an alkaline bath and an $O_3/O_2$ mixture, the efficiency was 99.64% and 99.37% and $NO_x$ concentration 25 and 60 ppm respectively for the first and second pass.

In Run 9a through d are shown the results of recycling scrubber liquor to exhaustion. The efficiency in the first pass was 99.76% with a small drop off in the second and third passes. It is observed that when scrubber liquor is basic efficiency is high and the off gas $NO_x$ concentration is below 50 ppm. But, as the alkali becomes exhausted in the scrubber liquor (9d) the efficiency was drastically reduced to 95.85% and the $NO_x$ concentration rises sharply to 660 ppm.

The increase in efficiency in an alkaline bath is largely attributed to formation of $NaNO_3$ in solution according to the following neutralization reaction:

| (Base) in solution | | (Acid) in solution | | (In solution) | | |
|---|---|---|---|---|---|---|
| $NaOH$ | + | $HNO_3$ | $\longrightarrow$ | $NaNO_3$ | + | $H_2O$ |
| (Fairly high vapor pressure) | | | | (Low vapor pressure) | | |

The reaction is driven strongly to the right.

The results of Runs 6 through 9c may be summarized as follows:

1. The absorption efficiency of runs made in an 0.1 N alkaline bath with either $O_2$ or $O_3/O_2$ mixture with inlet $NO_x$ concentrations in the 6000-12,000 ppm range are between 99.2 to 99.7% and the off gas generally in the 30-60 ppm range.

2. It was not possible to thoroughly evaluate the effect of the $\frac{N_2}{O_2+O_3}$ gas volume ratio on absorption efficiency due to the small number of runs made.

TABLE 3

Summary of Results Set up #1, Oxidant introduced into toxic gas line stream at bottom of scrubber

| Run No. | Oxidant | Gal Vol. Ratio $N_2$ $O_3+O_2$ | Scrubber Liquor Composition | Inlet Gas Concen. ppm NOx | Off Gas Concen. ppm NOx | Pass No. | Absorp. Eff. % | Comments |
|---|---|---|---|---|---|---|---|---|
| 1a | $O_3/O_2$ | .282 | Plain $H_2O$ | 1950 | 70 | 1st | 96.4 | Tower 3/4 flooded |
| 1b | " | .282 | Plain $H_2O$ | 1925 | 83 | 2nd | 95.7 | Tower 3/4 flooded |
| 2 | " | .424 | Plain $H_2O$ | 7900 | 67 | 1st | 99.1 | Tower not flooded |
| 3a | " | .141 | 0.1 nNaOH | 2070 | 30 | 1st | 98.5 | Tower flooded |
| 3b | " | .141 | 0.1 nNaOH | 2000 | 20 | 2nd | 99.0 | Tower flooded |
| 4 | $O_2$ | .141 | 0.1 nNaOH | 3300 | 33 | 1st | 99.0 | Tower flooded |
| 5 | " | .424 | Plain $H_2O$ | 8700 | 118 | 2nd | 98.64 | pH=2.0 end of run |
| 6 | " | .424 | 0.1 nNaOH | 10,700 | 27 | 3rd | 99.75 | |
| 7a | " | .141 | 0.1 nNaOH | 6730 | 38 | 3rd | 99.43 | |
| 7b | " | .141 | 0.1 nNaOH | 5300 | 39 | 4th | 99.26 | |
| 8a | $O_3/O_2$ | .282 | 0.1 nNaOH | 7100 | 25 | 1st | 99.64 | |
| 8b | " | .424 | 0.1 nNaOH | 9600 | 60 | 2nd | 99.37 | |
| 9a | " | .424 | 0.1 nNaOH | 9800 | 23 | 1st | 99.76 | pH = 10+ |
| 9b | " | .424 | 0.1 nNaOH | 7500 | 45 | 2nd | 99.40 | pH = 10+ |
| 9c | " | .424 | 0.1 nNaOH | 12,250 | 45 | 3rd | 99.63 | pH=9.9 at start |
| 9d | " | .424 | Acidic | 11,100 | 660 | 4th | 95.85 | Acidic, (Bath exhausted) |

3. Though the 0.1 NaOH liquor scrubs out most of the $NO_x$ from the gas stream in the first pass, on recycling the alkali becomes quickly exhausted resulting in poor efficiency, thereafter.

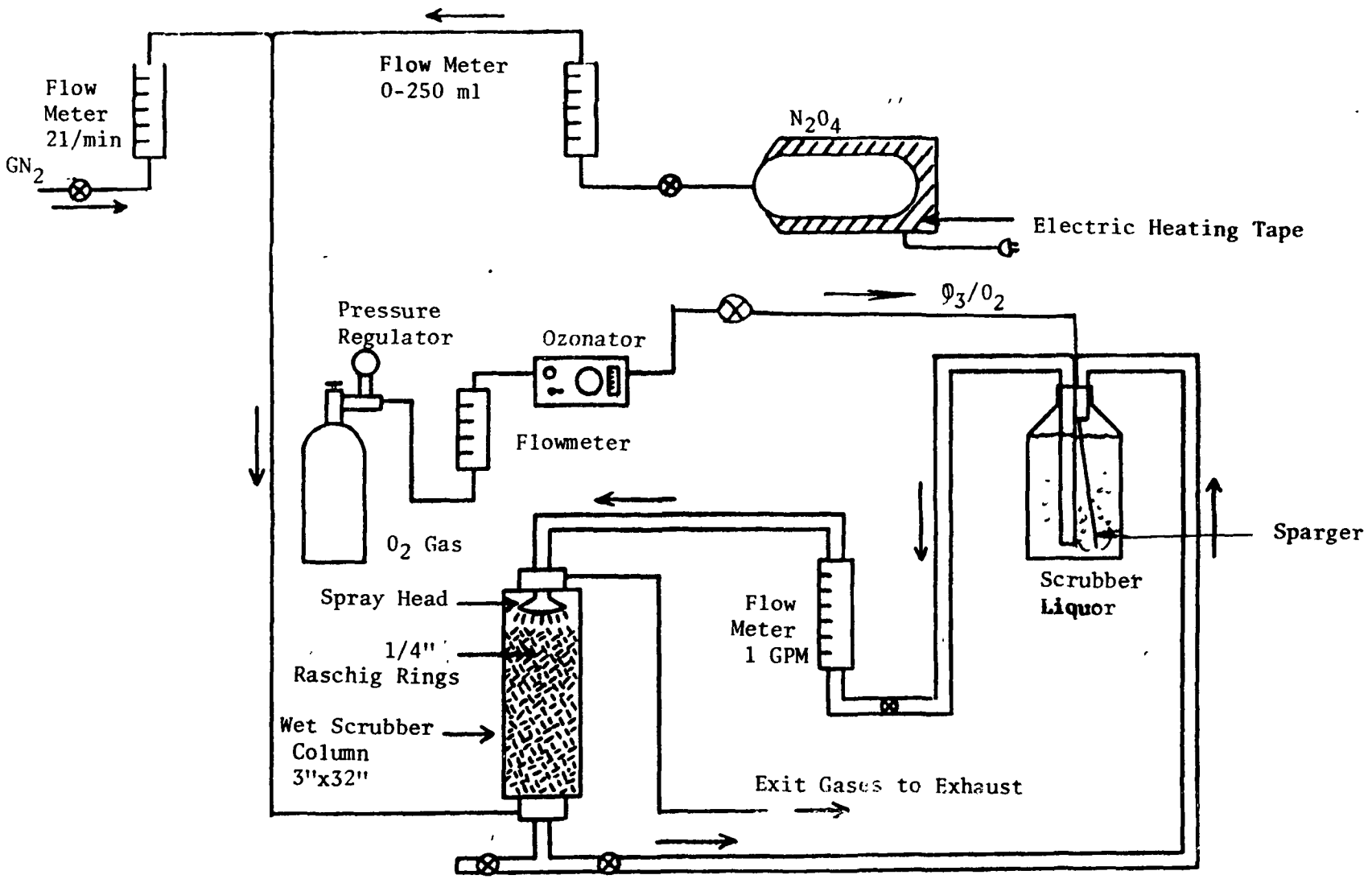
Set up 1 (Figure 6) was modified slightly as shown in Figure 7. Here the $O_3/O_2$ gas stream from the Ozonator was first passed through the scrubber liquor (instead of into the $N_2$-line) for 15-20 minutes to effect saturation. During a run the $O_3/O_2$ flow was continued into the liquor to maintain saturation of the oxidant. Four scrubbing runs were made, two in an alkaline bath and two in plain water. Results appear in Table 4.

The absorption efficiency in Run #10 was 99.7% made in an alkaline solution saturated with $O_3/O_2$. Absorption efficiency decreased to 99.0% in Run 11 with plain water and $O_3/O_2$.

In the oxygenated runs, absorption efficiency dropped to 96.1% (Run 12) in the plain water but was 99.3% in the alkaline solution (Run 13). The $NO_x$ concentration in the off gas was below 80 ppm in both alkaline runs (Runs 10 and 13) but was 200 ppm or higher in both plain water runs, once again showing the beneficial effect of an alkaline bath.

The difference in absorption efficiency between the $O_3/O_2$ and the $O_2$ runs (Runs 10 and 13) was only 0.4%. Such a small increase is hardly sufficient to warrant the extra effort involved in producing the $O_3$. This statement is true for the low flow, low volume conditions encountered in this experiment but may not be true for high flow/high volume gas inlet conditions.

As a consequence of these findings, a new series of runs was performed with the objective of determining the effectiveness of $O_2$ in the inlet gas stream at different $O_2$ concentrations. The results of these tests are described in section on scrubbing $N_2O_4$ vapors in alkaline baths and appear in Table 2 as Runs 8a through 8d.




SCHEMATIC SHOWING THE LABORATORY WET SCRUBBER (SET UP #2)

**Figure 7**

We gather from this that $O_2$ also provided suitable oxidative conditions for converting NO to $NO_2$. Therefore, it seems logical to forego use of $O_3$ in the system. The $O_3$ system would have inherent disadvantages such as substantially increasing operating costs and higher initial capital equipment cost to acomplish almost the same objective, i.e., an off gas emission of under 50 ppm.

Table 3 shows that when using scrubber liquor containing 0.1 NaOH with an oxidant gas the highest absorption efficiency obtained was 99.7%. Table 2 shows that efficiencies up to 99.8% may be obtained by using scrubbing liquor containing several percent NaOH without the presence of an oxidant gas.

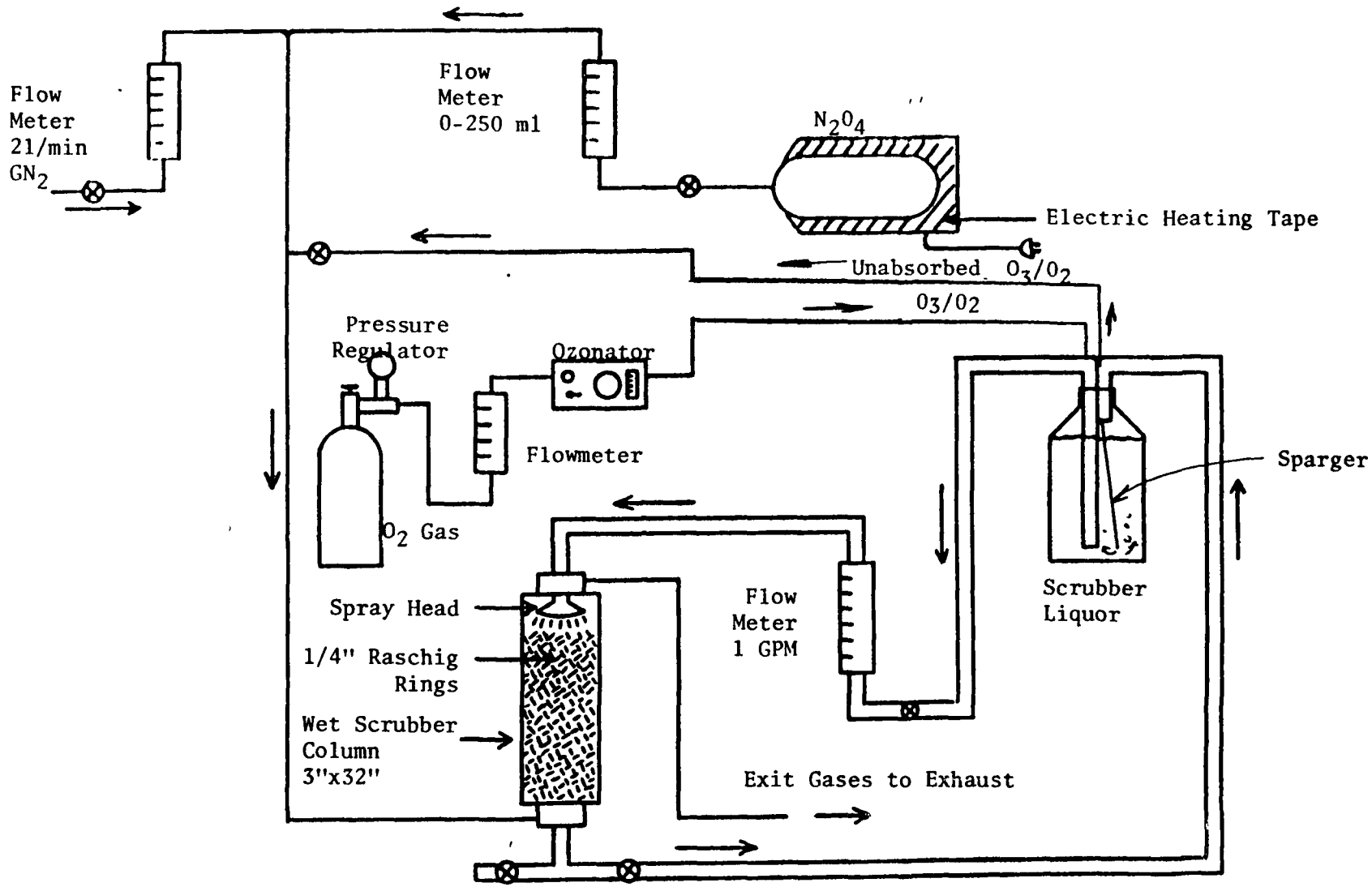
A second change in oxidant gas flow was made as shown in Figure 8. Here $O_3/O_2$ is passed through the scrubber liquor to maintain saturation and the unabsorbed gas stream is then introduced into the $N_2$ line upstream of the scrubber. This arrangement provides for both a liquid phase and a gas phase oxidation of NO. The results of two runs appear in Table 5. Absorption efficiencies were 99.4 and 99.2% very similar to that in run 13 in Table 4. No improvement in absorption efficiency was observed with this arrangement.

However, a disadvantage was observed. The $O_3/O_2$ gas in passing through the liquor picked up sufficient moisture to cause formation of an aerosol of $HNO_3$ in the line where it came in contact with the $NO_2$ stream. The aerosol condensed into liquid $HNO_3$ droplets on the inside surface of the tubing and at low points the gas line and generally interferred with the free passage of gases, attacked valve parts and interferred with the float of the flow meter.

TABLE 4

Summary of Results - (System #2 - Ozonated - Water introduced at top of Scrubber)

| Run No. | Oxidant | Gas Vol. Ratio $\frac{N_2}{O_3/O_2}$ | Scrubber Liquor Composition | Inlet Gas Concen. ppm NOx | Off Gas Concen. ppm NOx | Absorp. Eff. % | Comments |
|---|---|---|---|---|---|---|---|
| 10 | Ozonated Water | -- | 0.1N NaOH | 30,400 | 77 | 99.7 | |
| 11 | " | -- | Plain $H_2O$ | 32,700 | 330 | 99.0 | |
| 12 | Oxygenated | .141 | Plain $H_2O$ | 5,100 | 200 | 96.1 | No $O_3$ and no alkali |
| 13 | " | .141 | 0.1 N NaOH | 5300 | 39 | 99.3 | No $O_3$ |




SCHEMATIC SHOWING THE LABORATORY WET SCRUBBER (SET UP #3)

Fig.8

TABLE 5

Summary of Results - (System #3 - Ozonated $H_2O$ added at top of Scrubber and Ozonated $O_2$ introduced into TX Gas Stream at bottom of Scrubber)

| Run No. | Oxidant | Gas. Vol. Ratio $\frac{N_2}{O_3+O_2}$ | Scrubber Liquor Comp. | Inlet Gas Concen. ppm NOx | Off Gas Concen. ppm NOx | Absorption Efficiency |
|---|---|---|---|---|---|---|
| 14 | Ozonated $H_2O$ and Ozonated $O_2$ | .141 | 0.1N NaOH | 5800 | 20 | 99.4 |
| 15 | " | .141 | " | 4050 | 30 | 99.2 |

## 6. COMPARISON OF RUNS AND SET-UPS

Selected results from Tables 3, 4, and 5 were rearranged and appear in Table 6. It is seen that in plain $H_2O$ runs made in the presence of $O_3/O_2$ yielded slightly higher efficiencies (99.1%) than in the presence of $O_2$ alone. (98.6%)

Bearing greater significance is that in alkaline runs the efficiency difference of only 0.08% between the two conditions. This was an unexpected and welcome relevation. This shows that equivalent (or better) results can be obtained with only alkali in the scrubber liquor than with the presence of $O_3/O_2$ in the feed gas and only plain water in the scrubber liquor and probably operating at substantially lower expense.

It is evident from Table 6 that averaging absorption efficiencies from the three set-ups (oxidant introduction in three different ways) the following observations can be made:

1. In plain $H_2O$ runs, $O_3/O_2$ gives better results than $O_2$ in alkaline solution, i.e. 99.07 vs. 99.37% respectively.

2. $O_3/O_2$ in alkaline bath is slightly better than $O_2$ in alkaline solutions i.e. 99.52 vs 99.39% respectively.

3. The absorption efficiencies of set up #1 ($O_3/O_2$ fed directly to $GN_2$ line) and set up #2 ($O_3/O_2$ fed to scrubber liquor) are not significantly different.

TABLE 6

Comparison of Runs using an Oxidant

| | $O_3/O_2$ Plain $H_2O$ % Abs. Ef. | $O_3/O_2$ Alkaline Solution % Abs. Ef. | $O_2$ Plain $H_2O$ % Abs. Ef. | $O_2$ Alkaline Solution % Abs. Effic. |
|---|---|---|---|---|
| Set up #1 | 99.15 | 99.56 (avg. of 5 runs) | 98.64 | 99.48 (avg. 3 runs) |
| Set up #2 | 99.0 | 99.7 | 96.1 | 99.3 |
| Set up #3 | ---- | 99.3 (avg. of 3 runs) | ---- | ---- |
| Average % of col. | 99.07 | 99.52 | 97.37 | 99.39 |

## 7. SUMMARY FOR $O_3/O_2$ Runs

A comparison of scrubber efficiencies indicates that slightly higher efficiencies are obtained by using an oxidizing agent in the feed system than without the oxidizing gas. Also, the alkaline bath substantially increases scrubber efficiency to that obtained in plain water runs and permits recirculation of the scrubber liquor.

Temperature rise due to Reactions

The temperature rise during wet scrubbing was on the order of 1-3°C between inlet and exit scrubber liquor temperature. The temperature rise was attributed more to the chemical reaction of $NO_x$ with NaOH rather than to frictional factors or other factors. This almost negligible temperature rise is due to the large volume of scrubber liquor having a high heat capacity, and the relatively dilute NO concentration of generally under 1%. Such a low temperature presents little if any, danger and may be considered an adiabatic reaction.

## 8. CONCLUSIONS

The presence of $O_3/O_2$ in the $GN_2$-$N_2O_4$ feed gas to the scrubber demonstrated some NO oxidation effects and increased the absorption efficiency a few percent. However, the contact time within the scrubber was of too short duration to oxidize more than a small amount of the NO to $NO_2$ to permit better removal. Thus, the effectiveness of the $O_3/O_2$ in the scrubber feed gas is of insufficient magnitude to warrant its continued use.

Based on the above results on the $O_3/O_2$ runs, the following conclusions were drawn:

1. The absorption efficiency is increased from about 0.5 to 2.5% by operating with an $O_3/O_2$ oxidant in plain $H_2O$ runs without the oxidant.

2. Absorption efficiencies were in the 95 to 99% range in plain water runs which is below the level desired for the projected application of the system.

3. $O_3$ being a stronger oxidant than $O_2$ is slightly more effective in oxidizing NO than $O_2$.

4. The effluent $NO_x$ concentration from a scrubber tends to be insensitive to increases in inlet concentration. In effect, outlet concentration tends to remain fairly constant whereas overall collection efficiency changes when inlet concentration changes.

## 9. EFFECTS OF MASS VELOCITY OF GAS

In the plain $H_2O$ runs, the toxic gas flow rate was between 100 and 280 ml per minute, the $GN_2$ diluent gas between 1 liter and 3 liters per minute. The gas dilution ratio varied between 8.0 to 20 to 1. This was one way to control the concentration of the feed gas into the system. The resulting inlet toxic gas concentrations were in the range of approximately 1,000 to 46,000 ppm.

In the ozonated runs, the toxic gas flow rate was 200 ml per minute and $GN_2$ flow rate 1 to 2 liters/minute in most of the runs. The $O_2$ gas flow rate (used as $O_2$-source for $O_3$ generation) was 7.08 liters per minute. Thus, in the $O_3$ runs the gas dilution ratio was between 40 to 45 to 1, resulting in inlet toxic gas concentration from approximately 2000 to 12,000 ppm.

The maximum total gas flow rate in the laboratory runs was on the order of 10 liters per minute. Scrubber liquor flow rate usually was 0.15 GPM. Operation of the scrubber was straightforward under these conditions after allowing for a liquid seal of 4 to 4 1/2" to prevent gas escape through the bottom opening.

The runs were all performed at or near ambient pressure of one atmosphere. A pressure differential of about 10 - 20 inches of water was measured across the packed tower under typical operating conditions.

For scale up purposes, it was necessary to determine the maximum gas throughput without flooding ths system. Figure 9 shows that the system could accomodate approximately 2 CFM gas at .05 GPM liquid flow rate. Figure 9 also shows the operating point under maximum flows used for the runs. It is seen that the system was operated below both the gas and liquid flow rates thus allowing a safety factor for surges.

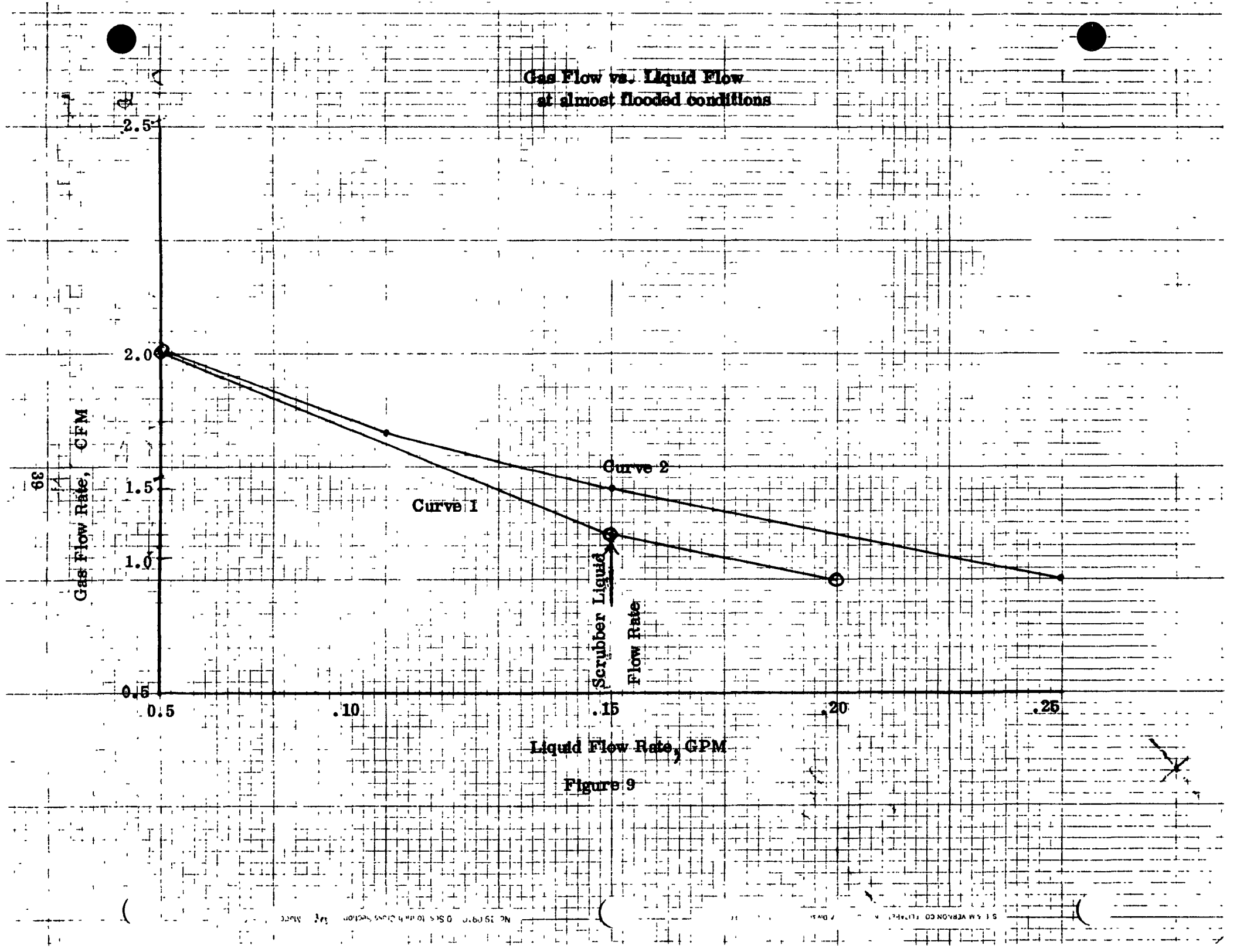

Gas Flow vs. Liquid Flow
at almost flooded conditions
2.5
2.0
1.5
1.0
0.5
Gas Flow Rate, CFM
Curve 1
Curve 2
Scrubber Liquid Flow Rate
0.5
.10
.15
.20
.25
Liquid Flow Rate, GPM

Figure 9

## 10. DISCUSSION OF $H_2O_2$ RUN RESULTS

The $H_2O_2$ runs were made with the same equipment and operating conditions as the preceeding runs except $H_2O_2$ was added to the scrubber liquor with two runs also containing alkali in solution.

Runs 1 and 2 (Table 7) show that the absorption efficiency of scrubber liquor containing 0.1N $H_2O_2$ to average about 90% which is similar to the efficiency of runs made with plain $H_2O$. The small amount of $H_2O_2$ was too dilute to rapidly oxidize NO. $2NO + O_2 \longrightarrow 2NO_2$ The rate of NO oxidation is known to be highly concentration dependent.

The efficiency of a run containing 0.25N $H_2O_2$ (Run 3) was approximately 2 percentage points higher than in Runs 1 or 2. The concentration of $NO_x$ in the off gas was 1335 ppm which is excessive.

In runs containing alkali plus $H_2O_2$ (Runs 4 and 5) the efficiency was increased by approximately seven percentage points above the plain $H_2O$ or dilute $H_2O_2$ runs and becomes comparable to previous alkaline runs. It is believed that the alkaline constituent (NaOH) rather than the oxidizing constituent ($H_2O_2$) provided a more favorable medium in which to reduce $NO_x$ of the incoming pregnant gas mixture. The $NO_x$ in the off gas was 143 ppm (Run 4) and 80 ppm (Run 5) - a significant improvement over the initial runs.

It is speculated that use of a suitable catalyst may have increased the effectiveness of $H_2O_2$ in the scrubber liquor, similar to the Cu++ catalyst observed and discussed in Phase 5 final report (February 1976) as applied to oxidation of MMH in ponds.

TABLE 7

| Run No. | Scrubber Liquor Composition | Inlet Gas ppm $NO_x$ | Off Gas ppm $NO_x$ | $NO_3$ in Liquid Effluent | Absorption Efficiency Percent | Comments |
|---|---|---|---|---|---|---|
| 1 | 0.1N $H_2O_2$ | 15,700 | 1450 | 890 | 90.8 | Efficiency is similar to plain $H_2O$ runs |
| 2 | 0.1N $H_2O_2$ | 16,900 | 1840 | 1470 | 89.1 | Efficiency is similar to plain $H_2O$ runs |
| 3 | 0.25N $H_2O_2$ | 18,000 | 1335 | 1340 | 92.6 | |
| 4 | 0.1N NaOH<br>0.1N $H_2O_2$ | 6,700 | 143 | 1890 | 97.8 | pH helps effic. |
| 5 | 0.1N NaOH<br>0.1N $H_2O_2$ | 13,700 | 80 | 5260 | 99.2 | Efficiency comparable to other alkaline runs. |

11. DESCRIPTION AND PURPOSE OF PROPOSED FULL SCALE SCRUBBER SYSTEM (MMC)

The effluent gases from existing ductwork first pass through a liquid-gas separator unit and then enter at the bottom of the wet scrubber through a gas distributor or manifold. (For $NO_x$-removal a second gas stream of $O_2$ is also introduced here, its purpose being to oxidize slightly soluble NO to soluble $NO_2$). The scrubbing liquor is introduced at the top of the scrubber through a shower-type nozzle to uniformly distribute the spray over the packing. The bed packing (Raschig rings or intalox saddles) provides a large surface area for intimate liquid-gas contact. In the bed gas absorption occurs by diffusion and complex chemical reactions. The airborne liquid droplets (entrainment) are removed from the gaseous stream by passage through a demister located conveniently. The cleaned gas ($N_2$ or He) containing small amounts of toxic gas (less than 100 ppm $NO_2$ or 10 ppm MMH) is vented to the atmosphere or is further diluted with air (fans) to reduce MMH/$NO_2$ concentration to below the acceptable level. This step simultaneously reduces the odor and color problems. The liquid stream is returned to the storage sump and is ready for recycling by means of a 1/2 hp centrifugal pump. The composition of scrubber liquor is maintained by replenishment or replacement with fresh solution

Description Packed-bed Scrubber (MMH or $N_2O_4$)

The wet scrubber consists of the following components:

1. A two foot diameter by seven foot high tower containing 3/4" raschig rings in intalox saddles, material - stainless steel or equivalent.
2. A 300 gallon liquid storage-recycle tank, stainless steel.
3. Recycle pump, 20 GPM capacity, chemical resistant construction.

4. Auxillary appurtanances as:

   a. Entrainment demister (cleaned gases)

   b. Pressure control/relieve valves

   c. Temperature indicators

   d. Piping/ductwork connectors

   e. Liquid-gas separator (entering vent gas)

   f. Flowmeters

   g. Sight glass

   h. Dilution fan

   i. Other, as required.

## 12. GENERAL DESCRIPTION OF COMPONENTS OF THE SCRUBBER SYSTEM TOWER (MMC)

The prototype scrubber tower will be two feet in diameter and seven feet high with conical or dished or other shaped end plates, 304 stainless steel construction. Gas inlet at bottom, gas exit at top. Near the tower bottom, provision is to be made for supporting the 1" packing material and for allowing the pregnant gas entry but preventing gas escape through the liquid drain by maintaining a gas seal with a few inches of $H_2O$. Piping and fittings shall be of corrosion resistant materials.

### Recycle Pump

A self priming centrifugal (or equal) 20 or larger GPM capacity, 1 hp pump, chemical resistant construction will be used to recirculate the scrubber liquor. A spray head at the discharge end will distribute the liquor in a uniform manner over the top of the packing. The pump can supply ~~can supply~~ the scrubber liquor the liquor storage tank on demand. Inlet (1 1/2") and discharge (1" or 1 1/4") openings are located to suit, 120 or 230 volt single or 3 phase, 1750 rpm, G.E. or equivalent.

### Liquor Storage Tank

The liquor storage tank shall have a capacity of about 300 gallons and be conveniently located with respect to the tower drain, 304 stainless steel construction or equal. The tank is provided with a drain cock and can have an auxiliary entry port for addition of chemicals or $H_2O$. Alternately, the tank can be filled or emptied with scrubber solution by means of the pump through manipulation of suitable valves.

Entrainment Demister

Though optional for the evaluation of the scrubber, the demister is desirable from the stand point of minimizing escape of corrosive liquid droplets. Also, possibly the demister effectiveness can be proved out simultaneously with the scrubber.

Liquid Gas Separator

The liquid gas separator is optional. Its use will prevent accidental intro - duction of liquid propellant surges into the scrubber.

Flow Meters

Liquid and gas flowmeters are necessary for controlling/measuring these fluids through the scrubber for obtaining velocities and mass flow rates.

Temperature indicators

Temperature indicators may be used for insuring against excessive temperature rises and to indicate temperature changes in the tower interior or effluent streams.

Sight Glass

A sight glass is of doubtful value and is optional but may aid in maintaining the liquid seal to prevent gas escape through the $H_2O$ drain.

Dilution Fan

The dilution fan (exhaust fan) is optional if dry scrubber is not used, but

may be required to dissipate heavy concentrations of toxic gases to safe levels or for reducing the pressure drop through the system. It can be the induced draft exhaust type, induction motor, weather proof, G.E. or equal.

Other Instruments, Inc.

Pressure relief valves are optional. Use of them will prevent excessive pressure buildup (unlikely) in the system.

A control panel is deemed an unnecessary expense for purposes of the scrubber evaluation.

Other instruments, as differential pressure guages, records, automatic shut-offs, if available can be applied but are not absolutely necessary for evaluation purposes, except, if the Cape wants them included.

## 13. SIZE OF LIQUID STORAGE TANK FOR NaOH SOLUTION

The size of storage tank required for the NaOH solution used for $NO_x$ scrubbing will be dictated by similar factors mentioned for the MMH scrubber.

The amount of $N_2O_4$ oxidizer vapors to be vented during the pad servicing operation was calculated previously to be 134 pounds (refer to page 190, Figure 43, Final Report, Phase 5). Using this figure as basis for the minimum amount of NaOH solution required for neutralization of $N_2O_4$ was found.

The equations representing the reactions are, (simplified):

$$N_2O_4 \rightleftharpoons 2NO_2$$
$$MW = 92$$

$$2NO_2 + 2NaOH \longrightarrow \underset{MW = 80}{NaNO_3} + NaNO_2 + H_2O$$

Thus, 92 parts $N_2O_4$ require 80 parts NaOH for stoichiometric neutralization if the above reaction is valid.

Then, 134 pounds $N_2O_4$ in vapor form requires $134 \times \frac{80}{92} = 116.6$ pounds NaOH. Allowing about 5% excess brings the amount to 123 pounds.

Converting weight to volume of 5% NaOH solution

$$\frac{123 \text{ lbs.}}{.05 \times 8.8 \frac{\text{lbs}}{\text{gal}}} = 280 \text{ gallons solution required per run.}$$

The minimum tank size, therefore, will be 300 gallons without any safety factors. A size safety factor of two will double the tank size (an alternate method is to have a provision for changing the contents of the storage tank during pad servicing).

The flexibility of multiple runs inherent in the MMH system does not exist in the $NO_x$ system due to the unduly large amount of $NO_x$ vapors to be absorbed compared to the small amount of MMH vapors. Further, tank sizing depends largely on the space allotment at the operating site.

Table 8 was prepared as a quick guide for selecting a tank to fulfill either minimum space requirement or with a size safety factor of two. The recommended NaOH solution strength for full flow testing, (CHAPTER 2), at Martin Marietta, Denver, is 5% in a 500 gallon tank with a safety factor of two. Based upon results obtained there, final recommendations will be made adequate for the purposes existing at KSC.

In the scrubbing experiments performed at F.I.T. satisfactory working strength of a scrubber liquor was found to be in the 4-6% contained NaOH range. A weaker solution requires a larger storage tank while absorption efficiency decreases slightly above 8% strength. Further, at high concentrations viscosity increases. As viscosity increases the flow characteristics of the solution over the bed material are affected adversely. Flow is slowed, flooding will occur sooner as gas volume and velocity is increased to the higher limits, i.e. (200 CFM).

A small amounts of $N_2O_4$ entrainment into the column in a closed system will not cause undue pressure or temperature rises.

Large $N_2O_4$ liquid surges into the scrubber are to be avoided by a suitable gas liquid separator in order to minimixe the instantaneous excessive back pressure problem.

Selection of the spray nozzle located at the top of the column should be of optimum design so as to minimize plugging. Though the reactants and products are very soluble, evaporation effects at the nozzle could cause local concentrations beyond the solubility limit of the materials contained.

Since about 120 pounds of NaOH are required for absorbing 134 pounds $N_2O_4$ calculation shows that a minimum of 3660 gallons of 0.1N solution would be required to scrub the vent gases in one shuttle pad loading operation. This is a prohibitive quantity due to the weight and space restrictions. For this reason, it was recognized that a stronger solution is adviseable.

TABLE 8

| Concentration NaOH Solution % | Volume of NaOH Solution(5% Excess), Gals. | Minimum Size Tank Gals. | Approx. Size Tank With Safety Factor of 2 Gals |
|---|---|---|---|
| 4 | 353 | 400 | 700 |
| 5 | 280 | 300 | 600 |
| 6 | 231 | 300 | 500 |
| 7 | 192 | 250 | 400 |
| 8 | 161 | 250 | 350 |
| 9 | 149 | 200 | 300 |
| 10 | 133 | 200 | 300 |

The absorption products formed in the scrubber are $NaNO_3$ + $NaNO_2$, both being very soluble in $H_2O$.* The danger inherent in plugging of nozzles or piping or of deposition in low spots by salt precipitation within the system during operation is thereby minimized.

*Solubility of $NaNO_3$ at 25°C is 92 grams per 100 cc $H_2O$ and of $NaNO_2$ at 15°C is 81 grams per 100 cc $H_2O$

Table 9
NaOH Density Data

| % NaOH by weight | Density @ 20° C | Grams/Liter | lbs NaOH Gal | Gals NaOH per Batch |
|---|---|---|---|---|
| 4 | 1.0445 | 41.7 | 8.70 | 353 |
| 5 | 1.0556 | 52.7 | 8.80 | 280 |
| 6 | 1.0667 | 63.9 | 8.88 | 231 |
| 7 | 1.0778 | 75.3 | 8.98 | 192 |
| 8 | 1.0888 | 87.0 | 9.07 | 161 |
| 9 | 1.0999 | 98.8 | 9.16 | 149 |
| 10 | 1.1110 | 110.9 | 9.25 | 133 |

# CHAPTER 2

# THE HIGH FLOW PACKED BED ABSORPTION EXPERIMENTS USING CAUSTIC SOLUTION AS A SCRUBBING AGENT FOR $N_2O_4$

## 1. DISCUSSION OF $N_2O_4$ RUNS AT MMC

Figure 10 shows results for Run 2 for $N_2O_4$ scrubber operation at 20 CFM in a four foot bed. The individual points indicate actual data points and the curve indicates the "best fitting" line as was obtained by the Least Squares Method. The results show rather poor absorption efficiencies ( 76-95%) with the four foot bed. Input concentrations were 862 to 5000 ppm $N_2O_4$ and effluents 200 to 253 ppm $NO_x$.

Figure 11 shows results for Runs 3, 10, 11, 12, and 15 performed at 20 CFM $GN_2$ flow rate in a seven-foot bed. (Run 12 was at 10 CFM). The absorption efficiencies were from 94.56 to 99.78% which are considerably higher than those obtained in the four-foot bed. This clearly demonstrated the beneficial effect of a greater bed depth. The 315 ppm effluent in Run 10 appears to be out of line with the others and it is believed that the scrubber conditions were unstabilized at the time of taking this sample and can be ignored.

In Run 15, the piping on the $MON_3$ source tank was modified to permit introduction of liquid $MON_3$ into the $GN_2$ gas feed line in order to increase the toxic gas to saturation levels. (It was found impossible to obtain very high concentrations of $NO_x$ with the gas feed setup after seven hours of trials). However, the high $MON_3$ concentration (410,000 ppm) could be maintained only for a duration of less than 10-12 minutes before the liquid supply in the small source tank became nearly exhausted, permitting a single reading at the very high level. The effluent in this run was 900 ppm and brown fumes were visible at the exit of the gas line.

Generally, the higher the imput concentration the higher the percent of absorption efficiency obtained.

The absorption efficiencies obtained on the MMC scrubber are somewhat lower than those obtained on the F.I.T. Laboratory model (usually 99.5 to 99.8% at moderate $N_2O_4$ inputs). A partial explanation is the larger surface area per

unit volume of the bed packing in the F.I.T. model as well as the longer contact times between the liquid-gas phases at lower gas flow rates permitting greater $NO_x$ absorption than was available on the full scale scrubber - especially at the high $GN_2$ flow rates.

Figure 12 shows the results obtained at 50 CFM $GN_2$ flow rate on runs 4 and 5 in a seven-foot bed. In Run 5, a mixture of 10% $O_2$ and 90% $N_2$ was used as a carrier gas to observe the effect of $O_2$ on absorption. Absorption efficiencies ranged from 88.0 to 97.56% - lower than in the 20 CFM runs. The $NO_x$ effluents were consistently in the 100-200 ppm range. This range is lower than in the four-foot bed but is higher than in the seven-foot bed at 20 CFM $GN_2$. Comparing Run 4 with a 3,600 inlet, it is evident that both sets of figures for percent absorption efficiency and concentration of outlet gases are nearly identical, thus showing no advantage with the 10% feed. (At F.I.T. only a small advantage was obtained with use of $O_2$ as was described elsewhere.

Figure 13 shows results obtained in Runs 6 and 7 at 100 CFM $GN_2$ in a seven-foot bed. The absorption efficiencies (about 83 to 96%) continued to decrease to below the 50 CFM values and the $NO_x$ outlet concentrations increased to approximately the 100 to 300 ppm range. As expected, the decline in absorption efficiency was attributed to the shorter contact time at higher flow rates of the gases in the scrubber.

Figure 14 shows results obtained in Run 8 at 200 CFM in the seven-foot bed. Absorption efficiencies ranged from about 73 to 88% with outputs in the 150 to 400 ppm range. The last two samples are considered to be atypical and should not be included. Again the shorter contact time results in poor efficiency and higher $NO_x$ concentration in the effluent gas.

In Figures 15, 16, 17, 18, and 19 the MMC data are plotted, outlet vs. inlet $N_2O_4$ concentration using the least squares method for a best fitted curve. These curves show that outlet concentrations rise with increasing inlet concentrations of $N_2O_4$.

## 2. ANALYSIS CONFIRMATION

The output gas concentrations, as obtained from either Drager tube or Olfactron instrument readings for $N_2O_4$, show a good correspondence to readings obtained by the wet chemistry method, in contrast to the MMH determinations. These readings appear in Table 11 of the Martin Report.

It is seen (Table 10) that over the three day testing period the solution strength decreased from 7.80% to 0.48%. At this point additional NaOH was added to bring strength up to 1.40%. Two short runs were made. At the conclusion of the testing the solution was discarded.

The amount of NaOH used up during testing was approximately 120 pounds which is sufficient to stochiometrically treat approximately 130 pounds $MON_3$. Our records show that the source tank (pig) was filled four times with $MON_3$. Weight figures are available for three pig fillings amounting to 95.25 pounds but excluded is the unknown weight of the first filling which would be between 25-35 pounds. This indicates a good correspondence with the stochiometric quantity.

Table 11 roughly summarizes the results of wet scrubbing $MON_3$ at MMC. It is evident that the trend for absorption efficiencies is to decrease with each increase in $GN_2$ flow rate; e.g. from 99.2% to 82% at flows from 10 CFM to 200 CFM. Figure 20 shows this graphically.

The run at 10 CFM was in a four-foot bed. This 10 CFM flow approximates the venting rate which occurs while pumping propellant at 80 GPM (equivalent to 10.7 CFM). Further, the efficiency was 99.2% which is close to the 99.6% efficiency obtained at the F.I.T. laboratory scrubber. At this condition, the full size scrubber and the laboratory scrubber show nearly the same efficiency. In a bed deeper than four-feet, it may be expected the efficiency would rise above the 99.2 level. The bed depth, however, would need to be increased more with each increase in flow rate to provide the desired highest efficiency, especially if a second stage day scrubber is not to be utilized.

TABLE 10
Strength of Scrubber Solution

| RUN DATE | RUN # | HOUR | % NaOH in SCRUBBER SOLUTION | COMMENTS |
|---|---|---|---|---|
| 8-26-76 | - | 0900 | 7.80 | Set up system, approx 123 lbs |
| | | 1000 | 7.68 | NaOH & 200 gals $H_2O$ |
| 8-26-76 | 1 | 1100 | 7.52 | |
| | 2 | 1300 | 5.96 | |
| | 2 | 1415 | 4.88 | |
| | 3 | 1440 | 4.60 | |
| | 4 | 1540 | 4.08 | |
| 8-27-76 | 5 | 0745 | 4.16 | |
| | 5 | 0935 | 3.77 | |
| | 6 | 1045 | 3.54 | |
| | 7 | 1345 | 3.13 | |
| | 7 | 1445 | 2.96 | |
| | 7 | 1530 | 2.67 | |
| 8-30-76 | 8 | 0930 | 2.48 | |
| | 8 | 1230 | 2.10 | |
| | 8 | 1345 | 1.76 | |
| | 13 | 1610 | 0.48 | Replenishment with 27 lbs NaOH, |
| | 14 | 1650 | 1.40 | plus 10 gals. $H_2O$ |
| | 15 | 1800 | 1.22 | |

TABLE 11

AVERAGED MMC DATA FOR $MON_3$ SCRUBBER RUNS (Exclusive of Bad Sampling)

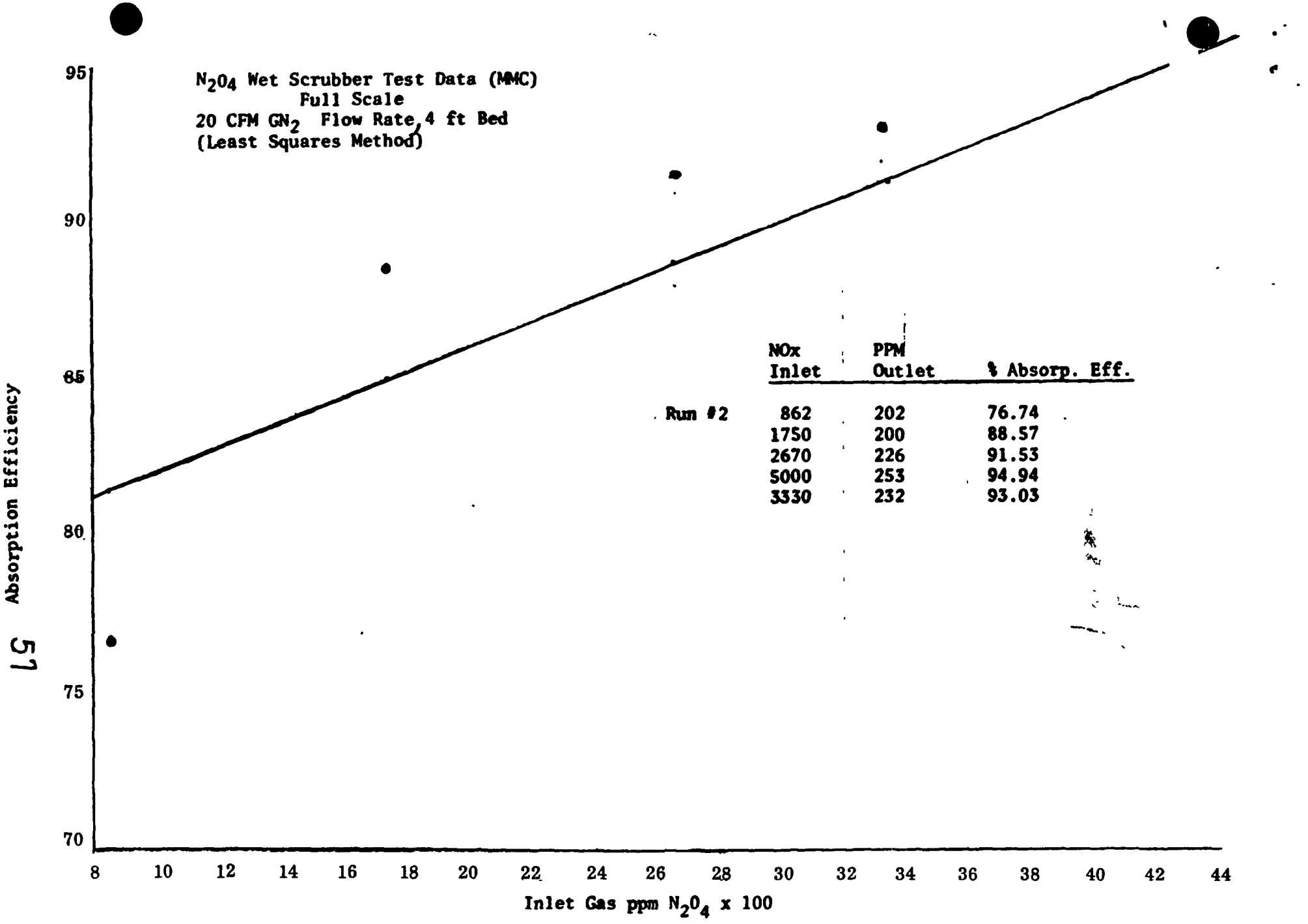
| $GN_2$ FLOW RATE CFM | BED DEPTH | % ABSORPT. EFFICIENCY | AVG. PPM NOx IN EXIT GAS | RANGE OF EXIT GAS PPM NO | COMMENTS |
|---|---|---|---|---|---|
| 10 | 4 | 99.2 | 110 | 68-151 | Approx flow rate during pumping 80 GPM |
| 20 | 4 | 92 | 222 | 200-253 | Bed Depth too shallow |
| 20 | 7 | 98.3 | 147 | 68-170 | |
| 50 | 7 | 94.2 | 160 | 102-193 | |
| 100 | 7 | 91.0 | 217 | 94-292 | |
| 200 | 7 | 82 | 278 | 159-390 | |

Similarly, the trend of the averaged $NO_x$ concentration as well as the $NO_x$ range in the gaseous effluent is to increase with each increase in $GN_2$ flow. Such a relationship was expected, as explained earlier, due to the contact time parameter.

## Design Changes

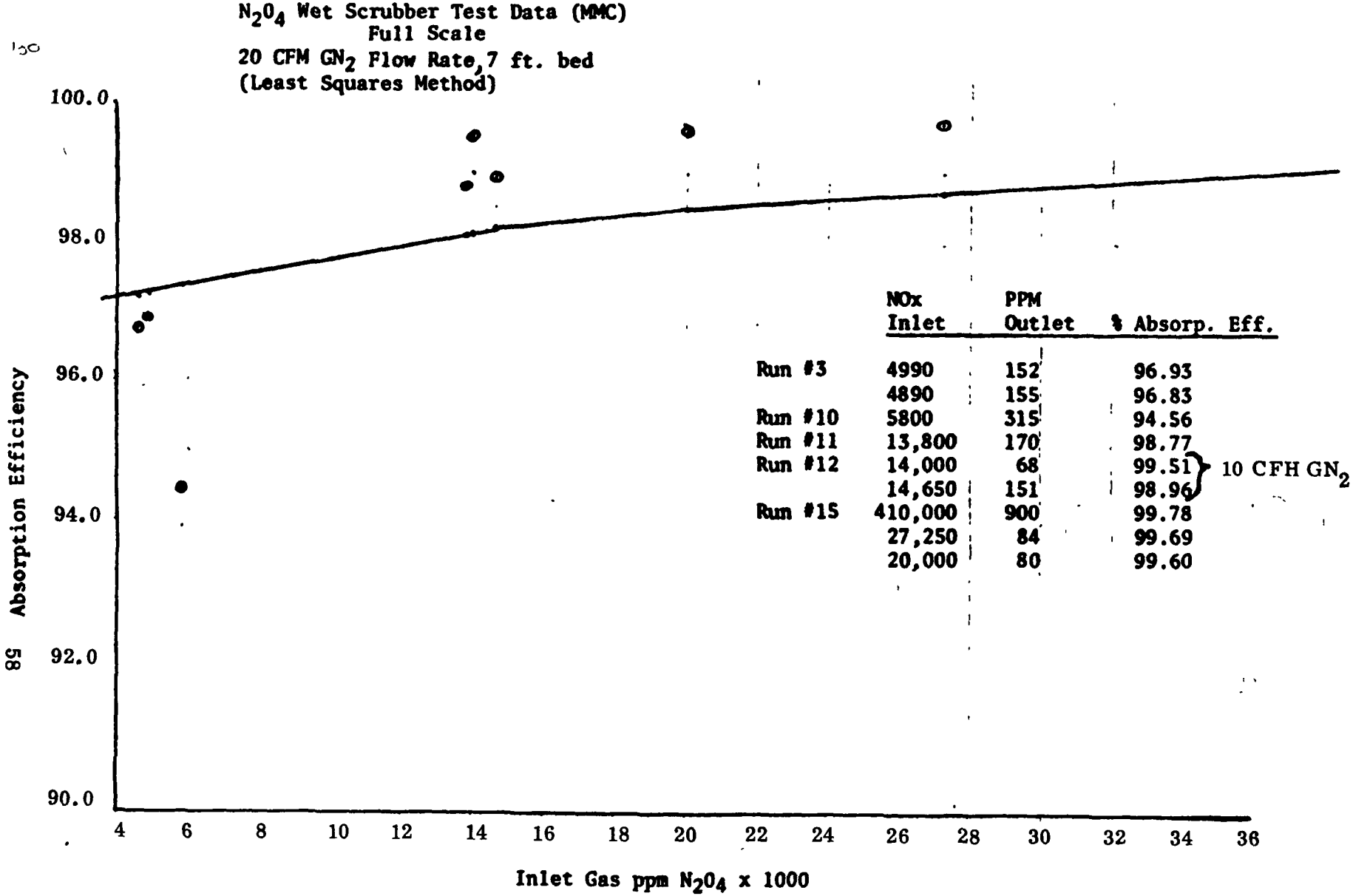
In order to improve the efficiency of the wet scrubber, several obvious design modifications, among others, are as follows:

1. Use smaller size bed backing, 1/2-3/4", instead of the 1" size, for larger surface area.
2. Deeper bed to allow longer contact time.
3. Larger diameter tower to accomodate higher capacity and lower gas velocity.
4. Liquor flow rate optimization and control capability.
5. More instrumentation and additional monitoring points for pressure, temperature and concentration changes, for rapid interrun changes.




| | NOx Inlet | PPM Outlet | % Absorp. Eff. |
|---|---|---|---|
| Run #2 | 862 | 202 | 76.74 |
| | 1750 | 200 | 88.57 |
| | 2670 | 226 | 91.53 |
| | 5000 | 253 | 94.94 |
| | 3330 | 232 | 93.03 |

Fig. 10




| | NOx Inlet | PPM Outlet | % Absorp. Eff. | |
|---|---|---|---|---|
| Run #3 | 4990 | 152 | 96.93 | |
| | 4890 | 155 | 96.83 | |
| Run #10 | 5800 | 315 | 94.56 | |
| Run #11 | 13,800 | 170 | 98.77 | |
| Run #12 | 14,000 | 68 | 99.51 | 10 CFH $GN_2$ |
| | 14,650 | 151 | 98.96 | |
| Run #15 | 410,000 | 900 | 99.78 | |
| | 27,250 | 84 | 99.69 | |
| | 20,000 | 80 | 99.60 | |

Fig. 11

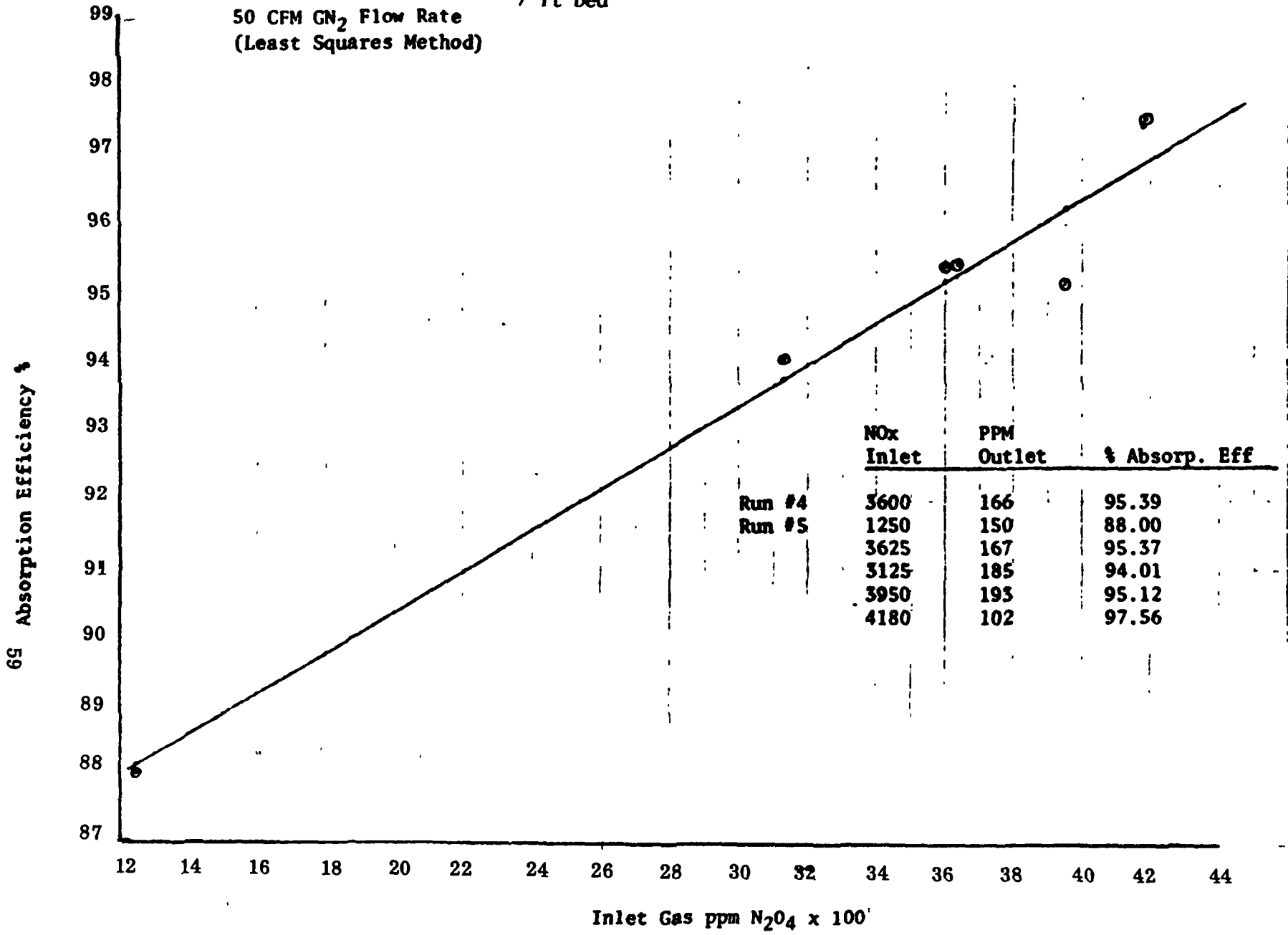

$N_2O_4$ Wet Scrubber Test Data (MMC)
Full Scale 7 ft bed
50 CFM $GN_2$ Flow Rate
(Least Squares Method)
99
98
97
96
95
94
93
92
91
90
89
88
87
69 Absorption Efficiency %
12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44
Inlet Gas ppm $N_2O_4$ x 100
NOx Inlet
PPM Outlet
% Absorp. Eff
Run #4 3600 166 95.39
Run #5 1250 150 88.00
3625 167 95.37
3125 185 94.01
3950 193 95.12
4180 102 97.56

Fig. 12

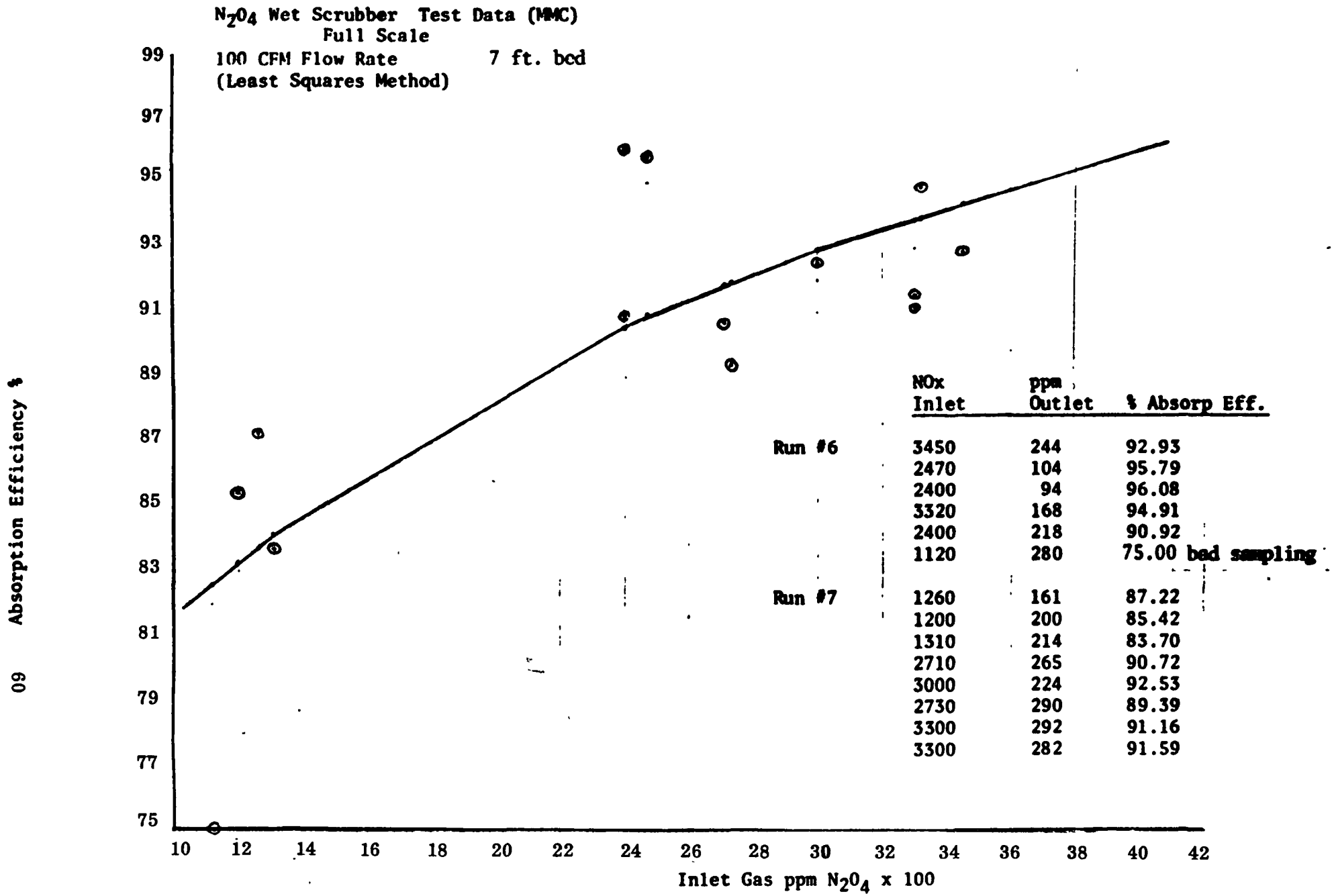
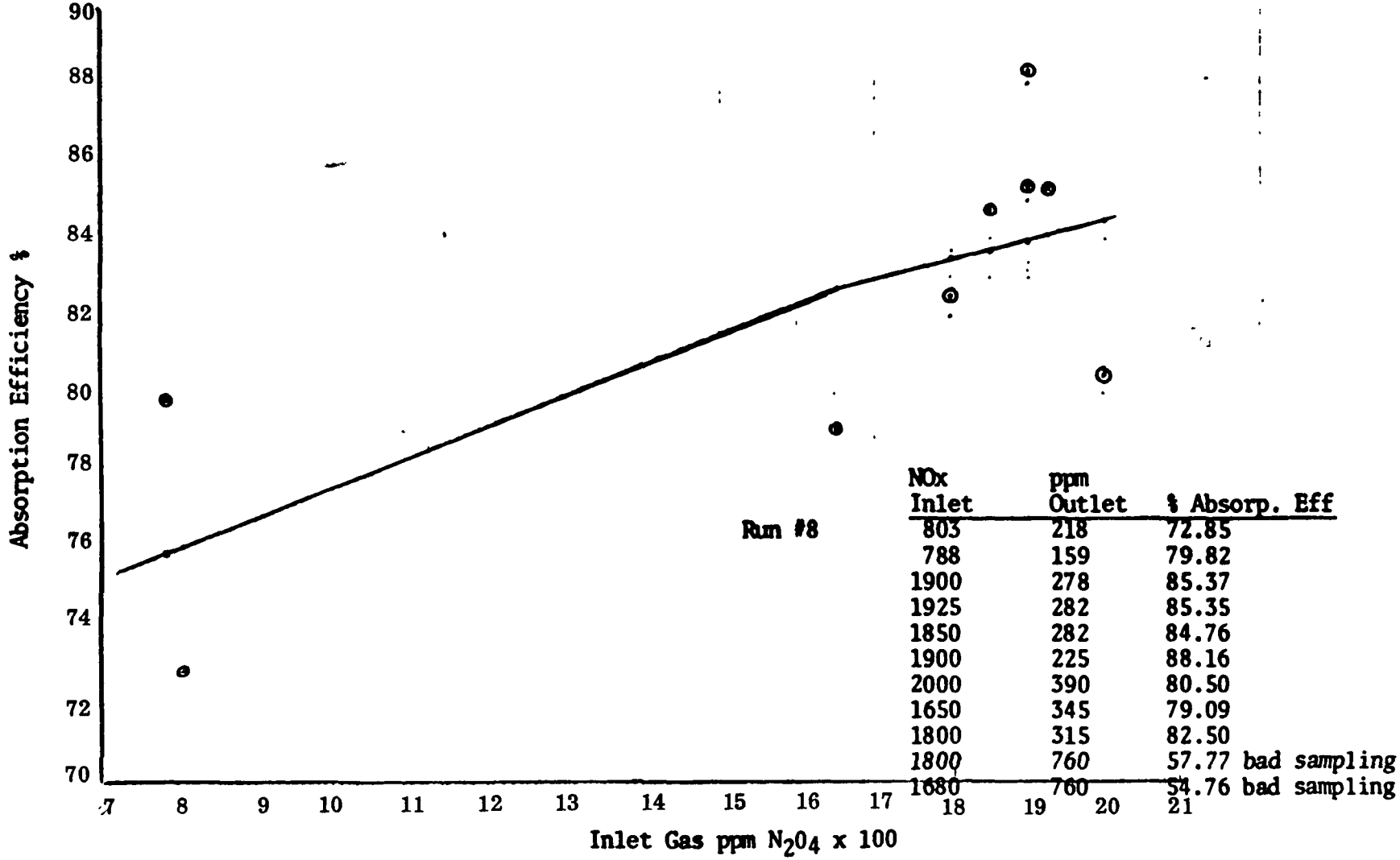

$N_2O_4$ Wet Scrubber Test Data (MMC)
Full Scale
100 CFM Flow Rate 7 ft. bed
(Least Squares Method)
99
97
95
93
91
89
87
85
83
81
79
77
75
09 Absorption Efficiency %
10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42
Inlet Gas ppm $N_2O_4$ x 100
NOx ppm
Inlet Outlet % Absorp Eff.
Run #6
3450 244 92.93
2470 104 95.79
2400 94 96.08
3320 168 94.91
2400 218 90.92
1120 280 75.00 bad sampling
Run #7
1260 161 87.22
1200 200 85.42
1310 214 83.70
2710 265 90.72
3000 224 92.53
2730 290 89.39
3300 292 91.16
3300 282 91.59

Fig. 13

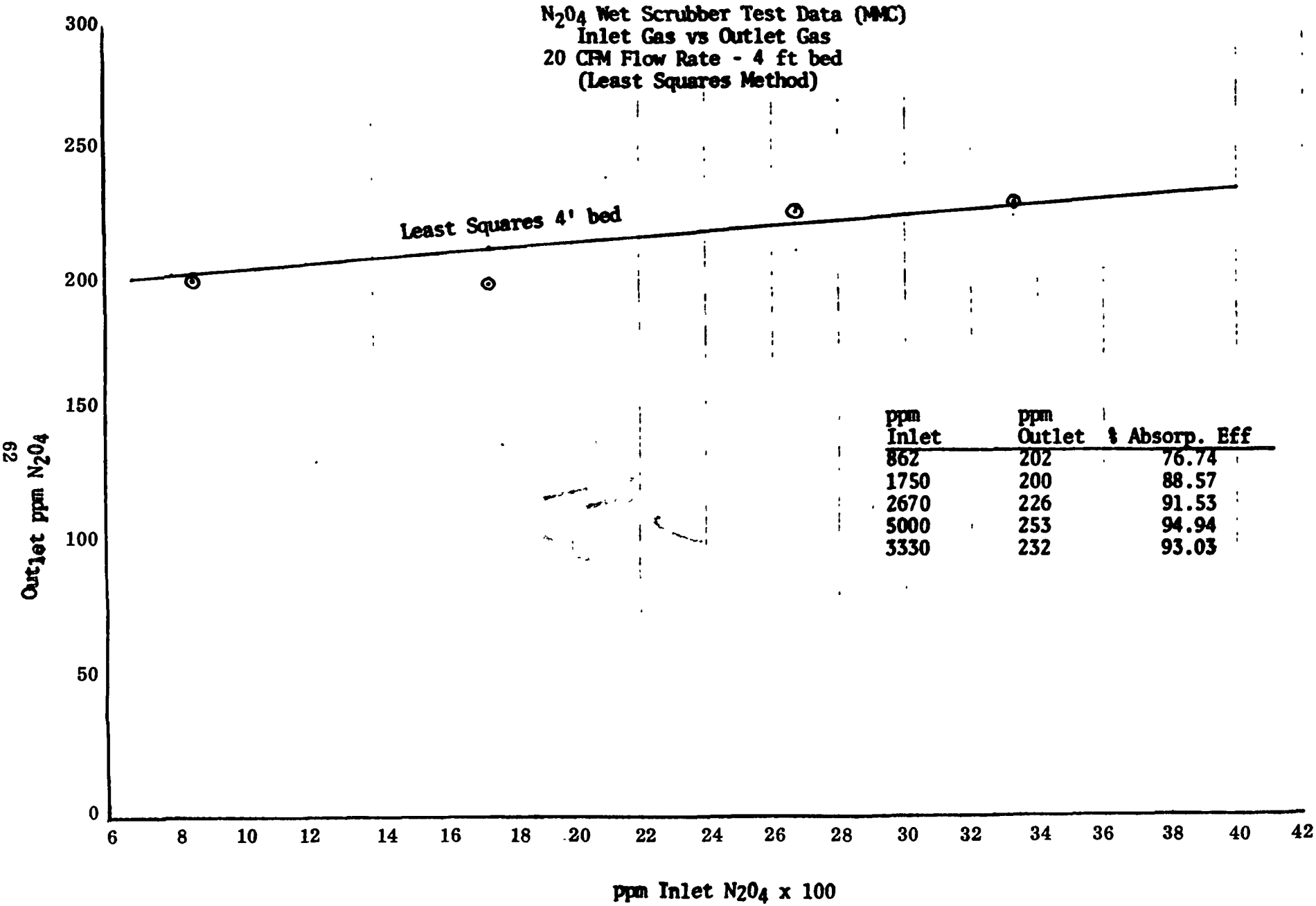
$N_2O_4$ Wet Scrubber Test Data (MMC)
Full Scale 7 ft bed
200 CFM $GN_2$ Flow Rate
(Least Squares Method)




Run #8

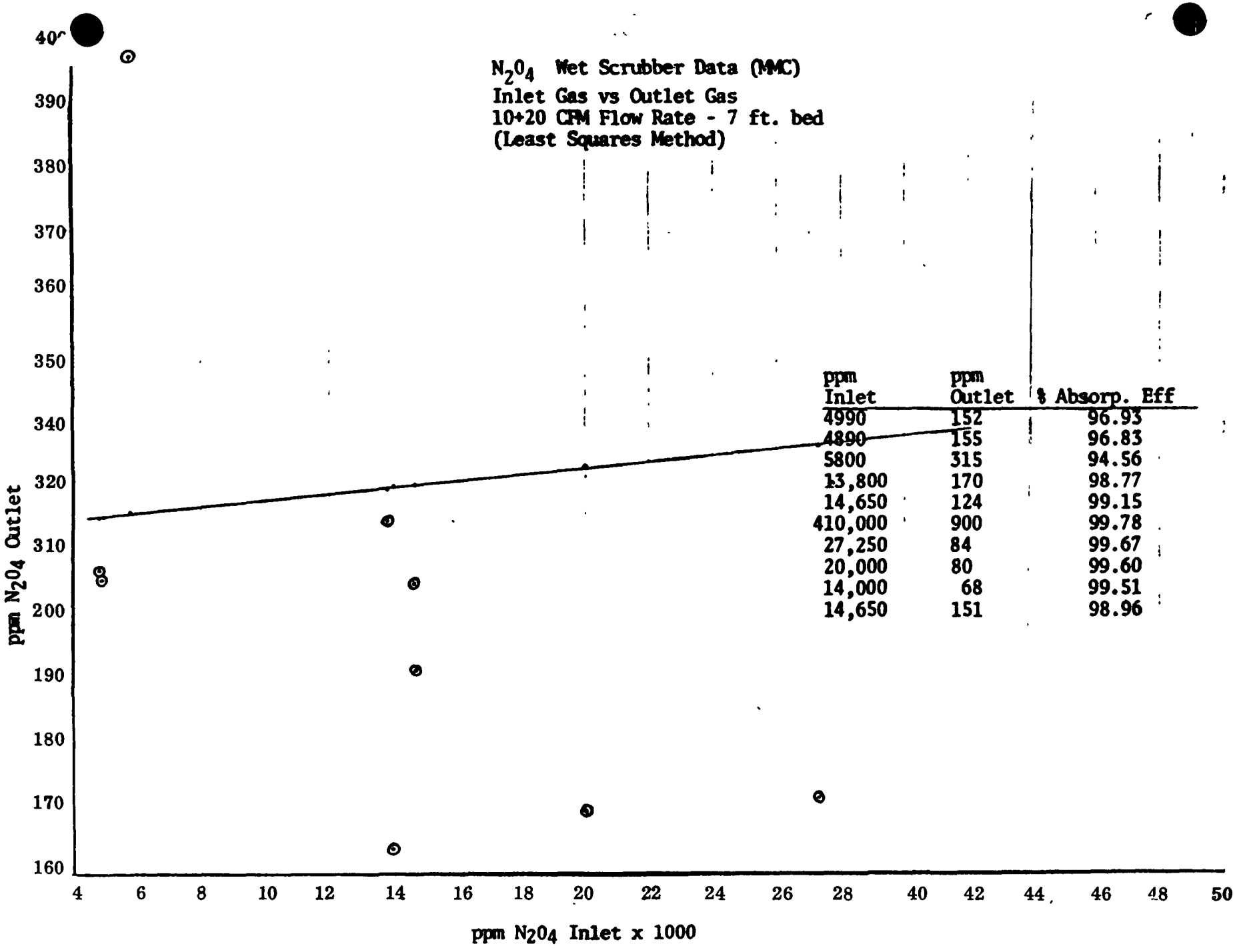
| NOx Inlet | ppm Outlet | % Absorp. Eff | |
|---|---|---|---|
| 803 | 218 | 72.85 | |
| 788 | 159 | 79.82 | |
| 1900 | 278 | 85.37 | |
| 1925 | 282 | 85.35 | |
| 1850 | 282 | 84.76 | |
| 1900 | 225 | 88.16 | |
| 2000 | 390 | 80.50 | |
| 1650 | 345 | 79.09 | |
| 1800 | 315 | 82.50 | |
| *1800* | *760* | 57.77 | bad sampling |
| 1680 | 760 | 54.76 | bad sampling |

Fig. 14




| ppm Inlet | ppm Outlet | % Absorp. Eff |
|---|---|---|
| 862 | 202 | 76.74 |
| 1750 | 200 | 88.57 |
| 2670 | 226 | 91.53 |
| 5000 | 253 | 94.94 |
| 3330 | 232 | 93.03 |

Fig. 15




| ppm Inlet | ppm Outlet | % Absorp. Eff |
|---|---|---|
| 4990 | 152 | 96.93 |
| 4890 | 155 | 96.83 |
| 5800 | 315 | 94.56 |
| 13,800 | 170 | 98.77 |
| 14,650 | 124 | 99.15 |
| 410,000 | 900 | 99.78 |
| 27,250 | 84 | 99.67 |
| 20,000 | 80 | 99.60 |
| 14,000 | 68 | 99.51 |
| 14,650 | 151 | 98.96 |

Fig. 16

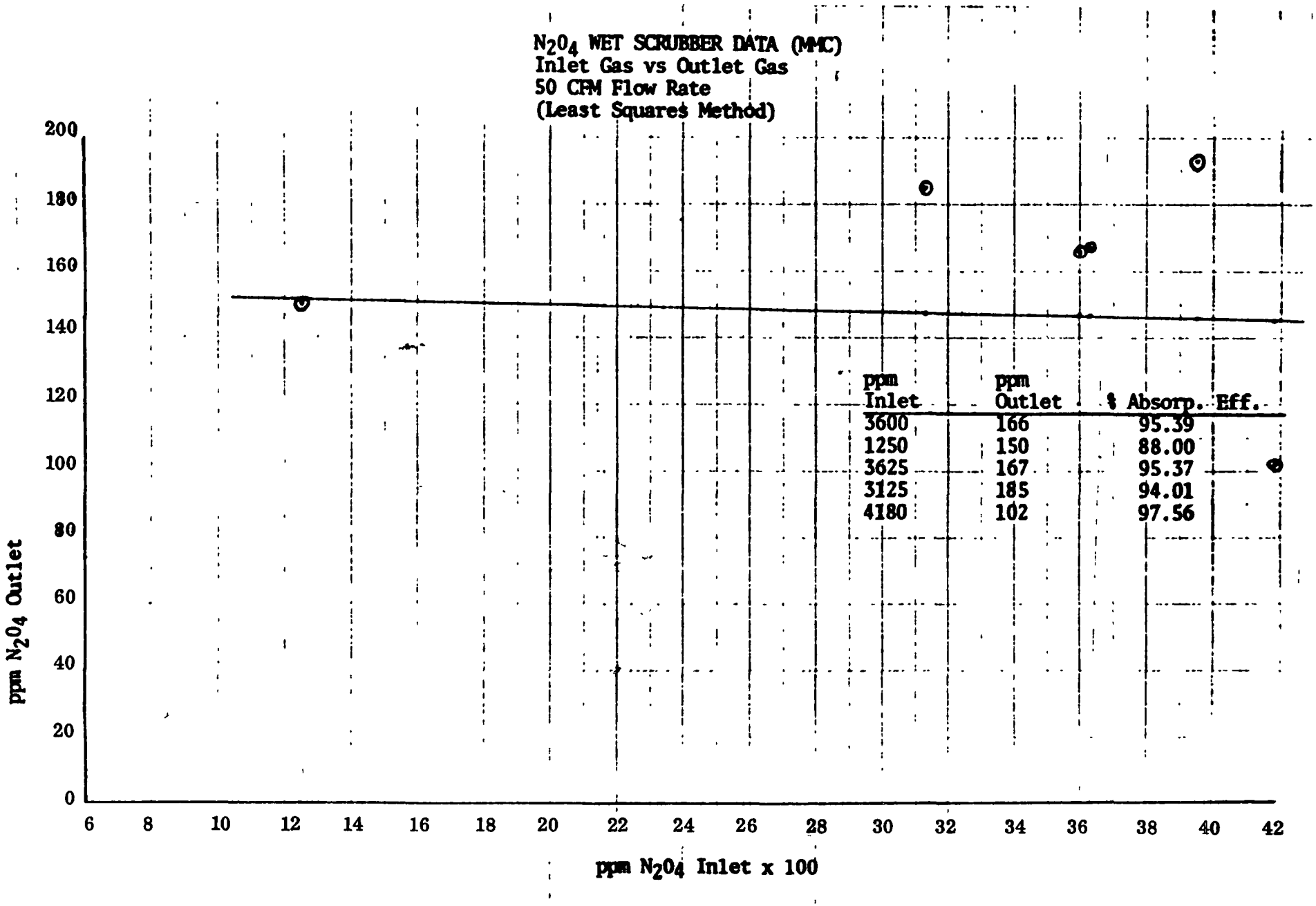
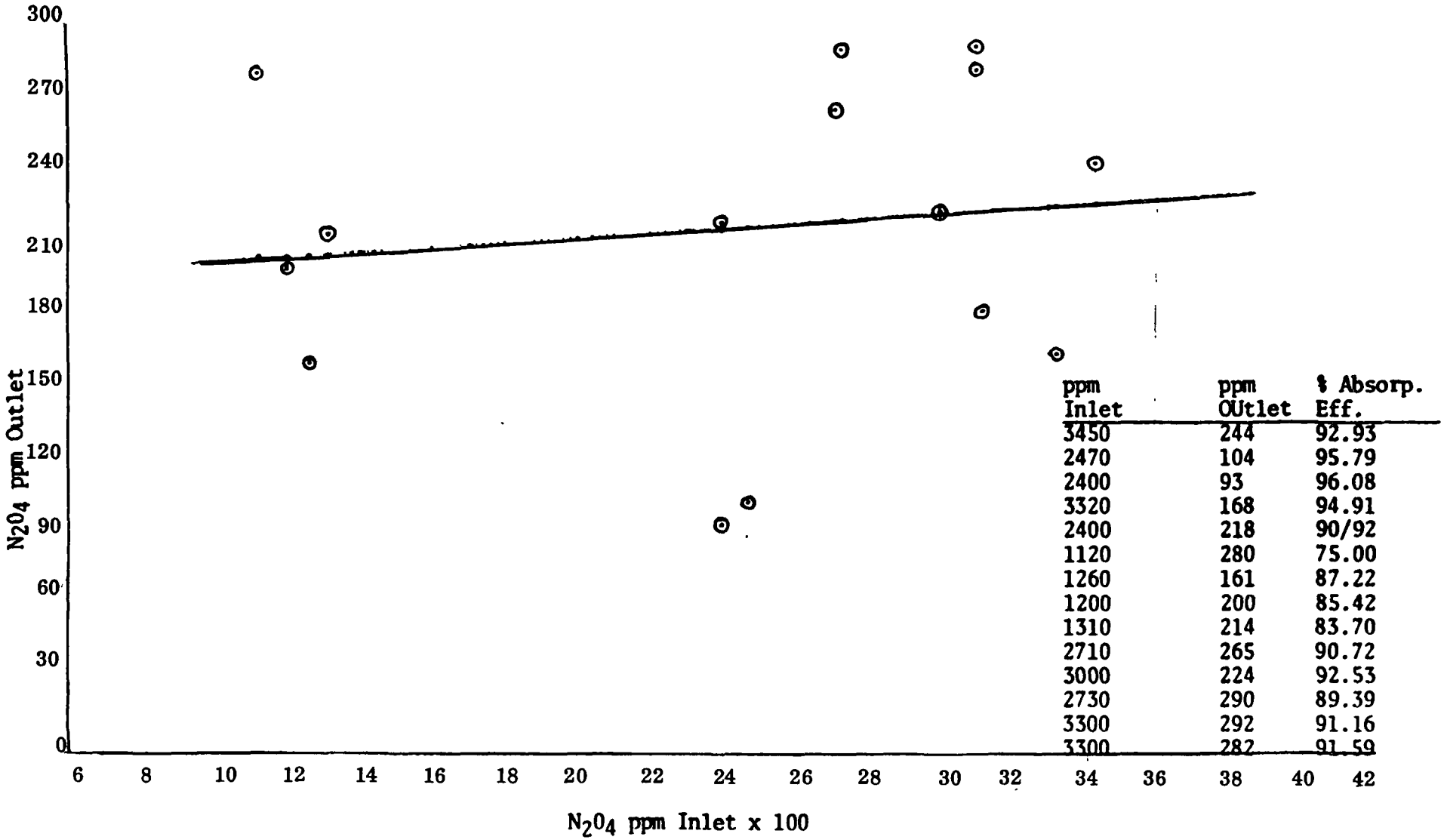

$N_2O_4$ WET SCRUBBER DATA (MMC)
Inlet Gas vs Outlet Gas
50 CFM Flow Rate
(Least Squares Method)
ppm $N_2O_4$ Outlet
ppm $N_2O_4$ Inlet x 100
0
20
40
60
80
100
120
140
160
180
200
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
ppm Inlet | ppm Outlet | % Absorp. Eff.
3600 | 166 | 95.39
1250 | 150 | 88.00
3625 | 167 | 95.37
3125 | 185 | 94.01
4180 | 102 | 97.56

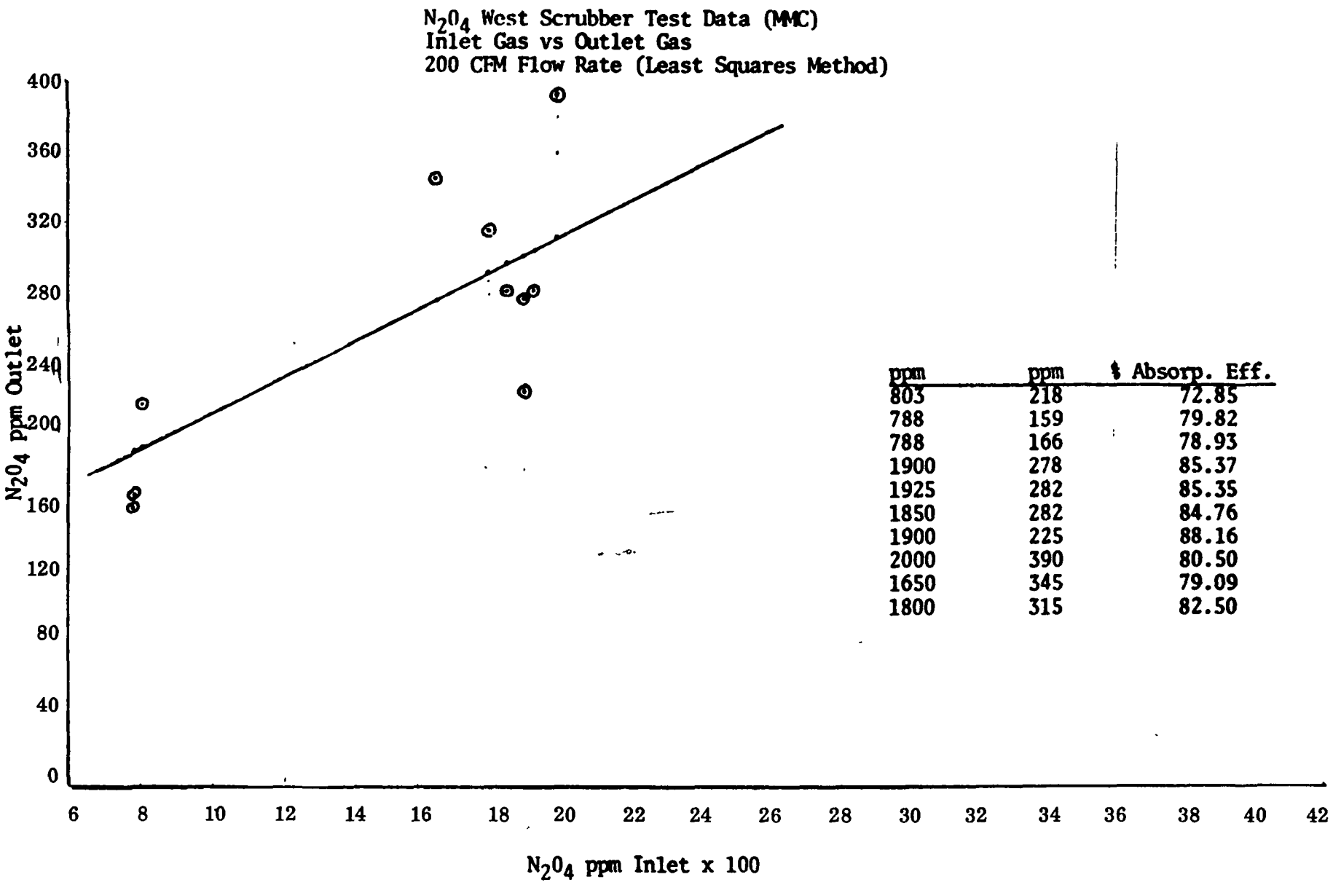
Figure 17

$N_2O_4$ Wet Scrubber Test Data (MMC)
Inlet Gas vs Outlet Gas
100 CFM Flow Rate
(Least Squares Method)




| ppm Inlet | ppm OUtlet | % Absorp. Eff. |
|---|---|---|
| 3450 | 244 | 92.93 |
| 2470 | 104 | 95.79 |
| 2400 | 93 | 96.08 |
| 3320 | 168 | 94.91 |
| 2400 | 218 | 90/92 |
| 1120 | 280 | 75.00 |
| 1260 | 161 | 87.22 |
| 1200 | 200 | 85.42 |
| 1310 | 214 | 83.70 |
| 2710 | 265 | 90.72 |
| 3000 | 224 | 92.53 |
| 2730 | 290 | 89.39 |
| 3300 | 292 | 91.16 |
| 3300 | 282 | 91.59 |

Fig. 18




| ppm | ppm | % Absorp. Eff. |
|---|---|---|
| 803 | 218 | 72.85 |
| 788 | 159 | 79.82 |
| 788 | 166 | 78.93 |
| 1900 | 278 | 85.37 |
| 1925 | 282 | 85.35 |
| 1850 | 282 | 84.76 |
| 1900 | 225 | 88.16 |
| 2000 | 390 | 80.50 |
| 1650 | 345 | 79.09 |
| 1800 | 315 | 82.50 |

Fig. 19

FULL FLOW WET SCRUBBER TEST
DATA FROM MARTIN MARIETTA

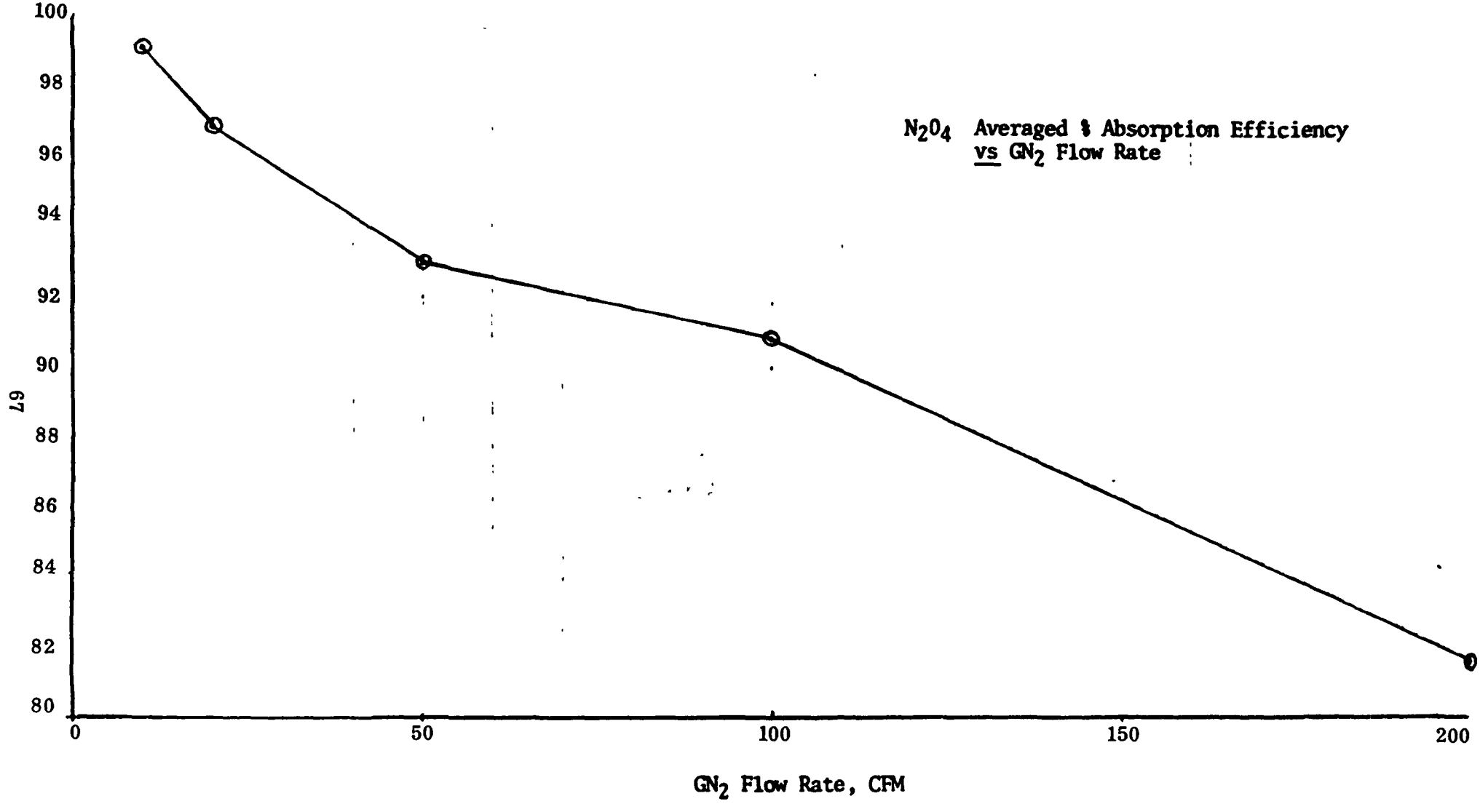



Fig. 20

## 3. CONCLUSIONS

Based on the above data, the following conclusions were made:

1. Though the 5 ppm effluent was not obtained directly in the single stage system, optimization by obvious design changes are believed feasible that will permit scrubber operation to go below the 50 ppm $NO_x$ level even under the worst conditions.

2. The percent absorption efficiency of the existing MMC scrubber and the F.I.T. Laboratory unit are approximately comparable only at the 10 CFM $GN_2$ flow rate.

3. Absorption efficiency is higher with the seven-foot bed than with the four-foot bed. Efficiency can be increased by a still deeper bed, a decrease in gas velocity through the bed, or increase in surface area of the bed packing.

4. Recirculation of a relatively small volume of an alkaline solution through the bed was a satisfactory way to reduce the weight and volume requirements for scrubber liquor necessary for scrubbing out $N_2O_4$ vented gases.

# CHAPTER 3

# THE LOW FLOW AND HIGH FLOW PACKED BED ABSORPTION EXPERIMENTS USING WATER AND SODIUM HYPOCHLORITE (NaOCl) AS A SCRUBBING AGENT FOR MONOMETHYL HYDRAZINE (MMH)

## 1. RESULTS AND DISCUSSION OF MMH SCRUBBER RUNS

The MMH absorption runs were made under varying conditions to determine efficiency for comparison of plain $H_2O$ runs with runs containing a solution of NaOH. It appears that scrubber efficiency is not significantly improved, if at all, by using this additive in the scrubber liquor.

Thus, the absorption of MMH vapor in a plain water scrubber was quite effective i.e., scrubber efficiencies on seven runs are all above 99% as shown in Table 12. The concentration of MMH vapor in the off gas range from 2.5 to 10 ppm when the inlet concentrations of MMH are 1100 to 2320 ppm. Based on seven runs, the averaged efficiency is 99.5%.

Two runs were made using a 0.1 normal NaOH solution as shown in Table 12. The averaged absorption efficiency was 99.7% and the off gas MMH concentration was 5 to 10 ppm.

The residual MMH concentration in the scrubber liquor in all the runs was in excess of 5 ppm and increased upward on recycling. On repeated recycling the MMH in both the off gas and the liquor increases as the absorption efficiency further decreases. The MMH in the off gas in all the runs in Table 12 is above the 0.2 ppm limit established as a desirable goal.

On the basis of these results and the emission limits, this mode (plain water or alkaline solution) scrubber operation for capturing MMH vapors from vent gases during shuttle loading is considered unsatisfactory.

TABLE 12

SUMMARY OF RESULTS MMH WET SCRUBBER RUNS

Plain $H_2O$ and Alkaline Water

| Run No. | Date | Composition of Scrubber Liquor | Inlet Gas PPM,MMH | Off Gas PPM MMH | MMH Residual in Scrubber Liquor,PPM | Scrubber Efficiency % | Pass | Comments |
|---|---|---|---|---|---|---|---|---|
| M-1 | 4/21 | Plain $H_2O$ | 2320 | 10 | 21 | 99.5 | 1st | |
| M-2 | 4/21 | Plain $H_2O$ | 1100 | 6.3 | 38 | 99.4 | 2nd | |
| M-1A | 4/22 | Plain $H_2O$ | 1850 | 4 | 6 | 99.7 | 1st | |
| #1 | 5/3 | Plain $H_2O$ | 1640 | 4 | 5 | 99.7 | 1st | |
| 1A | 5/3 | Plain $H_2O$ | 1250 | 10 | 12 | 99.2 | 2nd | |
| 1 | 5/6 | Plain $H_2O$ | 1810 | 2.5 | 8 | 99.8 | 1st | |
| 2 | 5/6 | Plain $H_2O$ | 2050 | 8 | 11 | 99.6 | 2nd | |
| | | | | | | | | Average Efficiency 99.5% |
| 3 | 5/6 | 0.1N NaOH | 2750 | 10 | 7 | 99.6 | 1st | |
| 4 | 5/10 | 0.1N NaOH | 3300 | 5 | 6 | 99.8 | 1st | |
| | | | | | | | | Average Efficiency 99.7% |

## 2. F.I.T. AND MMC EXPERIMENTS USING NaOCl AS A SCRUBBING AGENT FOR MMH

The absorption of MMH vapors in runs made with dilute solutions of NaOCl of varying concentrations in the scrubber liquor showed an effectiveness significantly higher than with the plain $H_2O$ runs. Table 13 shows that in seven first pass runs the absorption efficiency averaged 99.96%. The maximum off gas MMH concentration was 8 ppm in one case but generally the concentration was in the 1 or 2 ppm or fractional ppm level. The MMH concentration was never less than 0.3 ppm in any run.

All the runs were performed at very high MMH input concentrations, i.e., in excess of those realistically expected during a normal loading operation, wherein between 500 and 1000 ppm would be more typical, except for possible short term surges.

Two series of recycling runs were made starting with either 0.07 or 0.02 normal NaOCl solution. Periodically, a small amount of NaOCl was added to the recirculating liquor. The MMH concentrations of inlet and outlet gases was determined. These results appear in Table 13 as 8-series or 9-series of runs.

In the 8-series (A through F) it is clear that as the free NaOCl is used up in the scrubber liquor, the MMH concentration in the off gas (and liquor) increased to high and dangerous levels. This increase is by a factor of about 10 or more times higher than the figure shown for the non-exhausted bath in runs 1 through 7.

Similar comments apply to the 9-series of recycling runs. Due to the low initial amount of NaOCl (.02N) bath exhaustion occurred quickly during the second pass. The amount of NaOCl replenished was insufficient to convert the absorbed MMH during the operation.

These results indicate that relatively low MMH emission levels are possible in both of the off gas and the scrubber liquor provided a sufficiently high concentration

of NaOCl exists in the scrubber liquor to react with the vented MMH vapors. In contrast, results implicate that with plain $H_2O$ (or exhausted NaOCl baths) either a very high volume of scrubber liquor must be used to reduce MMH emissions to comparable levels or that recirculation of small volumes of scrubber liquor is not feasible if low MMH emissions are desired.

An obvious advantage in using NaOCl solution for scrubbing out MMH in vent gases is that the liquid effluent contains essentially none or only small amounts (a few tenths ppm) compared to about 20 ppm or more when plain $H_2O$ is used. Further, use of a dilute NaOCl solution will permit liquor recirculation without a build-up of MMH to a point where an odor is noticed or where absorption efficiency drops to an unacceptable level.

Run 10 was made using 3/4" quartz pebbles, in lieu of the 1/4" Raschig rings, with 1% NaOCl scrubber liquor. Though efficiency was 99.94%, a 4 ppm MMH off gas concentration was found. Interestingly, in this case the efficiency was not significantly different than in the "better" runs in spite of the lower interfacial surface area resulting from the bed material substitution. Under conditions of full flow this result would be different, i.e., with increased gas volume a rapid decrease in absorption efficiency is to be expected.

The amount of MMH in the off gas is in every case, above the 0.1 ppm OSHA limit, but not by much in several cases. In most instances, the natural mixing of the scrubber off gas with air in just 20 to 50 feet away would provide sufficient dilution to reduce MMH to below the OSHA limit.

At periodic intervals, after build up of salts in the liquor to a point of increased viscosity, the exhausted solution is dechlorinated and the pH adjusted to a suitable value. It may then readily be discharged into a sewer or stream without any pollutional consequence.

An acidic scrubber liquor was not tried due to lack of time.

## TABLE 13

## SUMMARY OF MMH/NaOCl RUNS

| Run No. | Amt. NaOCl In Sol'n | Inlet Gas, MMH PPM | Off Gas, MMH PPM | MMH Resid. In Liquor PPM | Absorp Eff % | Pass Number | Off gas Drager Check PPM | Comments |
|---|---|---|---|---|---|---|---|---|
| 1 | .05N | 5180 | 1.4 | 0.11 | 99.95 | first | 0 | |
| 2 | 0.6N | 3400 | 2.5 | 0.24 | 99.94 | first | 0 | |
| 3 | 1% | 6800 | 0.3 | ---- | 99.99 | first | 0 | |
| 4 | 5% | 3950 | 0.8 | ---- | 99.98 | first | 0 | |
| 5 | 2.5% | 4420 | 0.5 | ---- | 99.99 | first | 0 | |
| 6 | 5% | 5650 | 1.5 | 0.7 | 99.96 | first | 0 | |
| 7 | 1% | 6050 | 8.0 | 1.4 | 99.86 | first | 0.4 | Avg. = 99.95% for 7 runs |
| 8A | .07N initial | 7200 | 4.0 | 0.10 | 99.94 | first | 0 | |
| 8B | ---- | 7500 | 24 | 0.03 | 99.68 | second | - | |
| 8C | ---- | 5600 | 35 | 3.45 | 99.34 | third | - | Off Gas increases in MMH concentration |
| 8D | ---- | 4520 | 43 | 10.5 | 99.05 | fourth | 0.5 | Build up continues in gas and liquid efficients |
| 8E | ---- | 5300 | 55 | 131 | 98.96 | fifth | 2.0 | MMH conc. increases rapidly |
| 8F | ---- | 7700 | 70 | 69 | 98.99 | sixth | 5.0 | Added 300 ml NaOCl to liquor but amt. was insufficient to convert MMH |
| 9A | .02 | 3120 | 4 | .03 | 99.87 | first | - | |
| 9B | ---- | 5200 | 62 | 10 | 98.80 | second | - | Bath exhausted |
| 9C | ---- | 6150 | 90 | 11.4 | 98.54 | third | - | Replenished with 150 ml NaOCl solution-but insufficient to convert MMH |
| 10 | 1% | 8500 | 4.0 | ---- | 99.94 | first | - | Bed material was 3/4" quartz pebbles in lieu of rasching rings |

Total flow rate ($N_2$ + MMH) = 3 liters/min (all runs)

The MMH analyses were performed by the extremely sensitive p-DAB method, a wet chemical procedure. The off gas in some of the runs was checked by the Drager detector tube method. In most cases the latter method indicated undetectable amounts of MMH where small amounts were found by the wet method. It is believed that the Drager tubes are less sensitive to low concentrations of MMH than is true for $N_2H_4$ for which the tube filling is specific. Therefore, Drager readings were ignored and the results of the wet analysis were reported and believed.

Based on the above results the conclusion was drawn that NaOCl solutions are suitable to use for efficient absorption of MMH vapors to low (though not within the 0.1 ppm guideline limits) levels in both the gaseous and liquid effluents.

A recommendation is therefore made to further evaluate a scaled up version to a full size system using up to the maximum gas velocity and mass flow rates specified in the guidelines in order to determine the wet scrubber efficiency and emission levels at the typical and the maximum inputs - a feature not possible with the laboratory prototype.

## 3. CONCLUSIONS

For the laboratory system, the scrubber absorption efficiency with plain $H_2O$ was about 99.5%.

The gas absorption efficiency approaches nearly 100% with NaOCl solution. The residual MMH in the recycled liquor is usually 0.1 ppm or less by virtue of the reaction of MMH vapor with the NaOCl in solution

The gas absorption efficiency is changed almost insignificantly, if at all, by use of an alkaline scrubber solution under the conditions of the test.

The optimal NaOCl concentration in scrubber liquor is in the 1% to 5% range. The higher concentration allows a smaller liquor storage tank or alternately permits a greater number of runs before replenishment is required.

Construction and evaluation of a full size scrubber unit is strongly recommended under simulated field conditions.

These studies showed that in the wet scrubbing MMH systems:

1. Absorption efficiencies were higher when using a solution of NaOCl rather than plain $H_2O$.
2. MMH vapor emission was generally less than 5 ppm but only approached the 0.2 ppm TLV level.
3. The MMH concentration in the scrubber liquor is drastically reduced to a minute level, permitting direct discharge (after dechlorination) to a sewer. (actual measurements of MMH in liquid efficient were generally below 0.1 ppm)
4. Recirculation of scrubber liquor is feasible, thereby reducing the large volume of $H_2O$ necessary in once-through-systems.

However, uncertainties exist with respect to the following:

1. Emergency situations, as large spills, were not considered in this study.
2. How best to treat the residual MMH in vented gas. (options exist, for example, air dilution fans at scrubber exit, etc.)

3. How to handle large MMH liquid surges into the bottom of scrubber (option, install liquid-gas separation unit).

## 4. DECOMPOSITION OF DILUTED NaOCl SOLUTIONS IN STORAGE

The purpose of this experiment was to study the stability of diluted NaOCl solutions when stored in open or closed containers. Specifically, percentage decomposition is to be determined by analyzing for residual $Cl_2$. The strength of solutions is to be in the range specified for wet scrubbing of MMH vapors.

### Procedure

Two sets of diluted NaOCl test solutions were prepared in 1 liter quantities each for testing over a period of time. In the first set the initial residual $Cl_2$ concentrations were 0.55, 1.3, 2.8 and 5.2% These solutions were stored in screw capped glass bottles on the laboratory bench where diffused sunlight shone on them for approximately two hours per day. Aliquots were taken daily during the work week for $Cl_2$ analysis for a period of 32 days. The residual $Cl_2$ was determined by the iodometric method as given in the 13th edition of "Standard methods for the Examination of Water and Wastewater". The results appear in Figure 21 and Table 14.

The second set of test solutions was treated as above except the initial $Cl_2$ concentrations were 1.2, 2.0, 4.2 and 7.9%. These were stored for 21 days in large mouthed plastic containers. The results appear in Figure 22, and Table 14.

### Discussion

As the curves in Figure 21 show (not too plainly) all the test solutions stored in closed glass containers showed some decomposition in storage after 32 days. Generally, the more highly concentrated solutions showed a higher percentage of decomposition than the lower concentrations as appears in Table 14. Thus, the 5.2% solution decomposed 11.5%, the 1.4% solution only 7.6%. Such an amount of

decomposition is not excessive considering the storage conditions. The amount of decomposition after seven days storage was essentially nil in some cases or very little in others. It is a known fact that light, particularly sunlight, causes free $Cl_2$ to evolve. In a dark closed system the amount of decomposition of a NaOCl solution can be expected to be significantly reduced.

As Figure 22 shows, all the test solutions stored in open plastic containers have decomposed about three to four times as much as those stored in closed containers in spite of the shorter storage period. This is to be expected because of the adverse storage conditions. The sunlight and exposure to atmosphere enhanced evaporation of $Cl_2$. Actually, the amount of decomposition (9.4%) for the 1.2% solution is surprisingly small. Such adverse conditions would not exist in the scrubber operation.

TABLE I4
RESULTS OF STORAGE TESTS

| % Resid. $Cl_2$ in Closed Containers | % Decomposition After 32 days Storage | % $Cl_2$ in Open Containers | % Decomposition After 21 days Storage |
|---|---|---|---|
| 0.55 | 1.8 | 1.2 | 9.4 |
| 1.4 | 7.6 | 2.0 | 20 |
| 2.9 | 14.0 | 4.2 | 35 |
| 5.2 | 11.5 | 7.9 | 58 |

Conclusions: Based on the above date, the following conclusions are drawn:

1. Diluted (.5-5% $Cl_2$) NaOCl solutions stored in capped glass containers decomposed slowly over a period of 32 days. Percentage decomposition is small after 1 week storage.

2. The amount of decomposition in a 2.8% solution (approximately working strength in scrubber) was about 14% in the 32 day storage period.

3. Diluted (1-8% $Cl_2$) NaOCl solutions in open plastic containers decomposed fairly rapidly when stored for 21 days. Again percent decomposition was greater in the higher percent solutions.

4. The operation of an MMH vapor scrubber would not be greatly affected by the small amount of decomposition of the NaOCl solution if stored for periods of up to one month or longer in closed tanks.

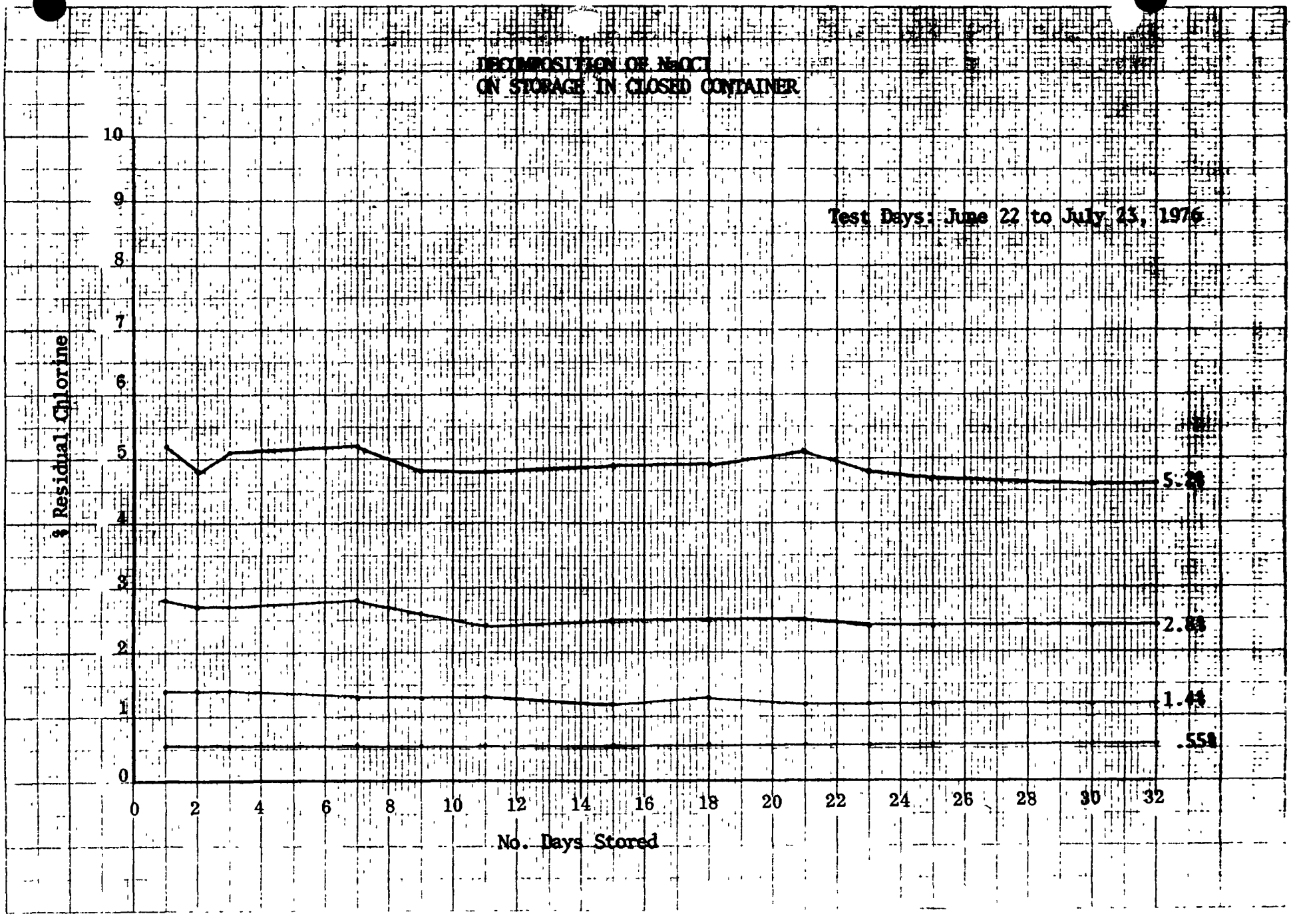

DECOMPOSITION OF NaOCl
ON STORAGE IN CLOSED CONTAINER
Test Days: June 22 to July 23, 1976
% Residual Chlorine
No. Days Stored
0
1
2
3
4
5
6
7
8
9
10
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
5.28
2.88
1.44
.558

Fig. 21

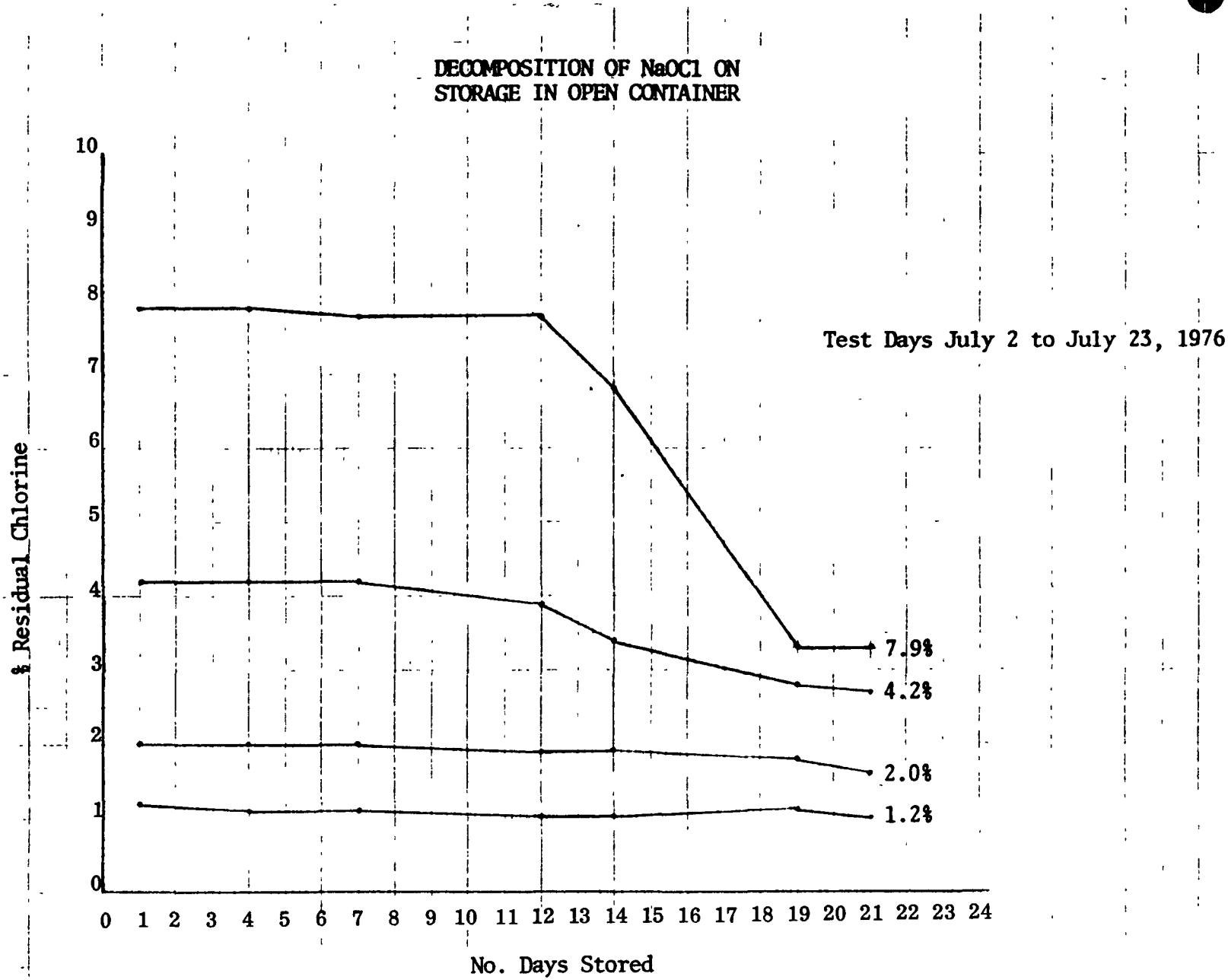

DECOMPOSITION OF NaOCl ON
STORAGE IN OPEN CONTAINER
Test Days July 2 to July 23, 1976
% Residual Chlorine
No. Days Stored
7.9%
4.2%
2.0%
1.2%
0 1 2 3 4 5 6 7 8 9 10
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24

Fig. 22

## 5. SIZE OF STORAGE TANK FOR NaOCl SOLUTION

The size storage tank required for the MMH scrubber will be dictated by the amount of MMH vapor to be absorbed, the concentration of the neutralizing agent in the scrubber liquor, certain design considerations, the safety factor applied against unexpected occurences, and the specific requirement of applicable local and state air pollution control code.

The amount of MMH expected to be vented during a shuttle loading operation was calculated previously to be 1,381 g which is equivalent to 3.04 pounds (refer to p. 189, Figure 42, Final Report, Phase 5). Using this figure as basis, the minimum amount of NaOCl required for neutralization of MMH can be found. A worst case situation is also calculated.

An equation for the partial oxidation of MMH to $CH_3OH$ is:

$$CH_3N_2H_3 + 2NaOCl \longrightarrow CH_3OH + N_2 + H_2O + 2NaCl$$

One mol of MMH requires two mols of NaOCl. On a weight basis this is equivalent to 3.24 lbs. NaOCl per pound of MMH. A slight excess of NaOCl is recommended to ensure complete decomposition of the MMH. Allowing a 5% excess, brings the amount of NaOCl to 3.5 lbs. per one pound of MMH.

To decompose 3.04 lbs. MMH will consume 10.6 lbs. NaOCl on a dry basis. This amount is contained in 106 lbs. of a 10% NaOCl solution - the commercially available product. This amount is equivalent to 11.7 gallons of 10% NaOCl solution.

However, in a worst case situation, if 10 lbs. of MMH vapor has to be destroyed, 32.4 lbs. of NaOCl (dry) or 324 lbs. of 10% solution are required. Including a 5% excess brings the total to 340 lbs. of solution. Converting weight to volume at 9.05 lbs/gal/, shows that 37.4 gallons of a 10% NaOCl solution are required to destroy 10 lbs of MMH.

Dilution of the 10% solution is necessary to a working strength of 1-5%. Contact of liquid MMH with 10% NaOCl is to be avoided as they react violently as described by tests in the Phase 3 report.

Tables 15 and 16 were prepared to show the strength and volume of scrubber solution, amount of NaOCl solution, the approximate number of runs possible and 10 lbs. or 3 lbs. MMH loadings vs. the minimum size of the storage tank. As shown a 250 to 300 gallon storage tank will permit two or more runs, depending on the loading, without either solution replacement or replenishment of the scrubber liquor.

The recommended scrubber solution storage tank is a minimum of 250 gallons. This size will still permit 100 gallons or more of solution for the liquid coverage of bed packing and to all the recirculatory system piping.

The recommended strength of the scrubber solution is to start at 3% contained NaOCl. A fresh bath will have capacity to destroy 21 lbs. MMH (or provide a safety factor of two for the worst case) and/or allow seven runs of 3 lbs. MMH to be made without bath replacement.

MMH entrainment into the packed column in a closed system presents a lesser problem of absorption than a large sudden surge of MMH vapor due to the high miscibility of MMH with water. The vapor must first pass through the gas-liquid interface in molecular fashion, whereas the small liquid droplets instantly coalesce with water. As the MMH droplets dissolve, they are neutralized by the dissolved NaOCl, if not immediately, soon after they reach the main body of scrubber liquid in the liquor storage tank.

Large MMH liquid surges into the scrubber, on the other hand, are to be avoided by a suitable gas-liquid separator. Even though the scrubber liquor is fairly diluted it contains a strong oxidizing agent which reacts vigorously (forming a large gaseous volume) with MMH causing unpredictable back pressures.

TABLE 15

Scrubber Solution Volume, Concentrationand Storage Tank Size for Treating 3 lbs. MMH

| % Desired Concentr. of NaOCl in Scrubber Liquor | Volume of Scrub Liquor Required for 3 lbs of MMH Gal | Suggested Minimum Size Storage Tank, Gal | Volume 10% NaOCl Solution Gals | Volume $H_2O$ Gal. | Approx. * Number of Runs |
|---|---|---|---|---|---|
| 1 | 103 | 300 | 30 | 270 | 3 |
| 2 | 51.7 | 250 | 50 | 200 | 5 |
| 3 | 34.5 | 250 | 75 | 175 | 7 |
| 4 | 25.9 | 250 | 100 | 150 | 10 |
| 5 | 20.7 | 250 | 125 | 125 | 12 |



TABLE 16

Scrubber Solution Volume, Concentration and Storage Tank Size for Treating 10 lbs MMH

| | | | | | |
|---|---|---|---|---|---|
| 1 | 374 | 750 | 7.5 | 675 | 2 |
| 2 | 187 | 400 | 20 | 320 | 2 |
| 3 | 125 | 300 | 90 | 210 | 2.4 |
| 4 | 93.5 | 300 | 120 | 180 | 3 |
| 5 | 74.8 | 300 | 150 | 150 | 4 |

* Reliance should not be placed on this table for the number of runs possible, rather, it is mandatory to analyze the scrubber liquor for available $Cl_2$ to determine when replenishment or solution replacement is necessary.

## 6. CALCULATION OF CAPACITY FOR AN MMH SCRUBBER

MMH is to be removed from vent gases containing approximately 0.05% MMH vapors by countercurrent scrubbing with a NaOCl solution at atmospheric pressure and ambient temperature. This system was determined to be the "best" system in a series of laboratory experiments described elsewhere. The scrubber efficiency desired is at least 99.95% in order to provide an MMH effluent of less than 0.2 ppm, if possible. However, such a high efficiency was found difficult to achieve in a single stage system.

The chemical engineering calculations on the capacity of gas absorption columns, as given in Perry, are based on simple material balances and on rates of absorption of the special gas-liquid system of interest. Where a small volume of absorption liquid must be used because of the space and weight limitations, as in the Shuttle application, the liquid is continuously recirculated over the packing surface. In the course of this work, the idea was in mind to select the scrubber design features so as to bring the MMH vapor and liquid phases into intimate contact to achieve the maximum efficiency and to reduce the toxic gas emission to the lowest possible level i.e., to 0.2 ppm MMH or less - which is below the levels realized in practice.

It is usual practice to employ a gas velocity through absorption columns of about 1 cf per second per sq. ft. cross section of the unpacked column at one atmosphere total pressure. To obtain such a velocity, calculations show that a two-foot diameter column will adequately provide for the 200 cfm venting and blow down requirement

$$\text{Gas velocity} = \frac{200 \text{ CFM}}{\frac{\pi D^2}{4} \times 60 \frac{\text{sec.}}{\text{min.}}} = 1.06 \text{ CF/sec./sq.ft.}$$

Such was the column diameter specified for the full flow evaluation tests at MMC in Denver.

## 7. MMC EXPERIMENTS USING NaOCl AS A SCRUBBING AGENT FOR MMH

Full flow evaluations of the wet scrubber for MMH were conducted by MMC in September 1976. The results of the tests are described in their test report #H 40679. The Martin data were formed into a set of nine tables which include the data points and least squares curves showing percent absorption efficiency vs. inlet gas concentration

Figure 23 shows results from test Runs 1, 4, 6, 7 and 8 for MMH scrubber operated at 20 CFM. The individual points indicate actual data for the four-foot and the seven-foot beds. The curves indicate the "best fitting" line as was obtained by the least squares method. The results show that absorption efficiency increases with increase in inlet gas concentration. Absorption efficiencies are higher in the seven-foot bed than in the four-foot bed. Outlet concnetrations of MMH do not exceed 5 ppm and are as low as 1 ppm as determined by wet analysis.

Figure 24 shows results from test runs 2 and 9 for 100 CFM $GN_2$ flow rate. Here, absorption efficiencies are higher for the four-foot bed and the outlet concentrations are less than 2 ppm MMH when the wet method of analysis is used, and less than 8 ppm MMH in the seven-foot bed. However, if the efficiencies are based on Drager readings the efficiencies are higher in the seven-foot bed than in the four-foot bed and these effluents then contain undetectable amounts of MMH.

Figure 25 shows results from test Runs 3 and 10 for 200 CFM $GN_2$ flow rate. The absorption efficiencies based on wet analysis are higher in the four-foot bed than in the seven-foot bed but the opposite is true if based on Drager readings. In Run 3 (four-foot bed) outlet concentrations are about 2 ppm MMH with both wet and dry methods of analyses. In Run 10 (seven-foot bed) outlet concentrations range from 1 - 9.5 ppm by the wet method, but only show 0 to 0.25 ppm MMH by Drager readings.

Figure 26 shows results from test run 5, for 430 CFM $GN_2$ flow rate with rather poor absorption efficiencies (87.5 - 97.86%). It is believed that possible $Cl_2$ contamination of the gas samples may have occurred from the visible entrainment carry over through the gas exhaust line to the sampling port resulting in fictitiously high MMH readings. A definite $Cl_2$ odor was noted in the proximity of the scrubber exhaust line. Drager readings indicated zero MMH in the effluent gas.

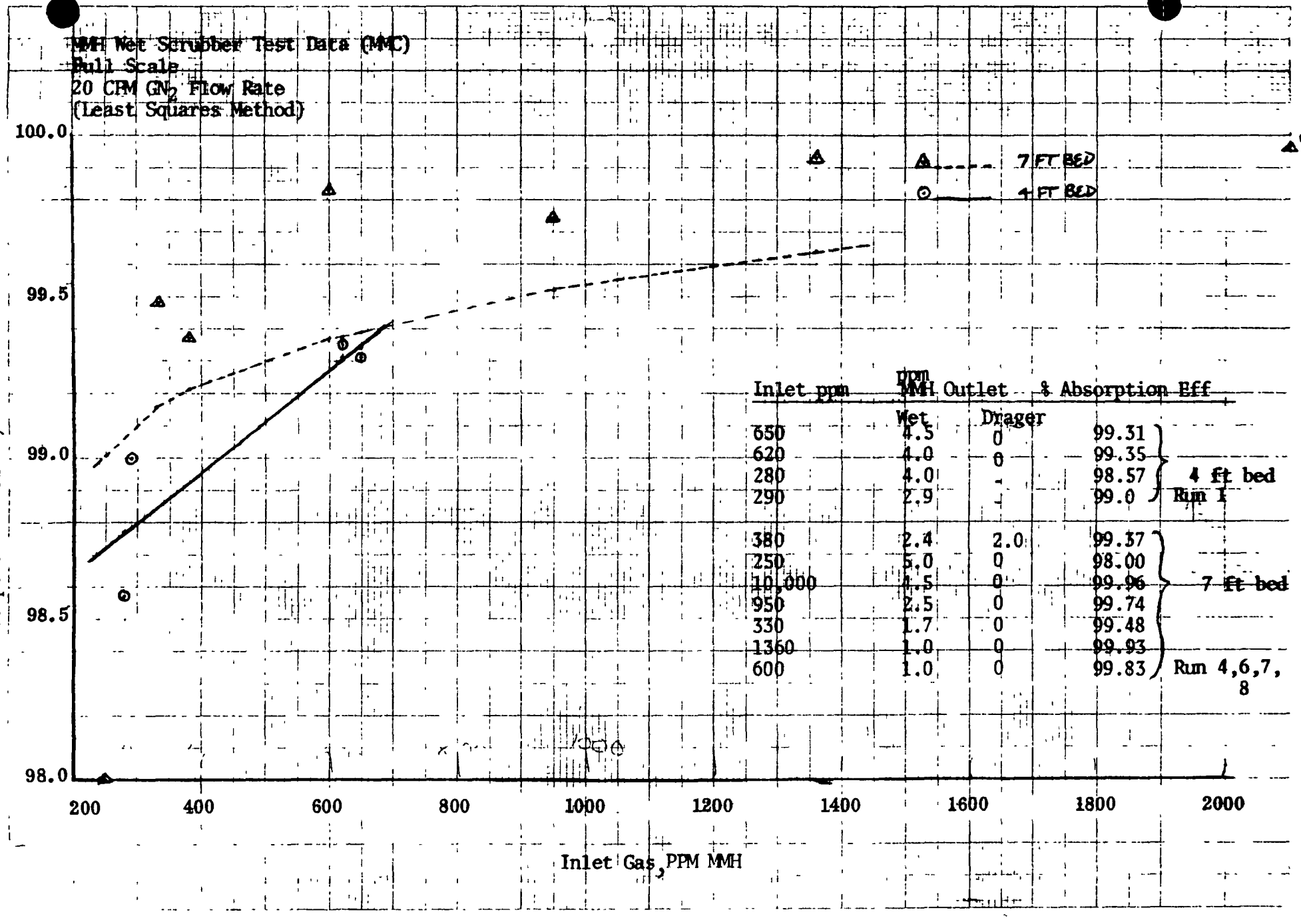
Entrainment

Only a fair agreement was obtained between the wet and dry methods for determination of concentrations of MMH in the scrubber effluents. The problem derived from the entrainment in the effluent and is explained below.

Great care was taken to keep the sampling syringes and laboratory glassware spotlessly clean in order not to contaminate the gas samples taken for analysis at MMC. It was noticed during sampling, particularly at the higher $GN_2$ flow rates (100, 200, 430 CFM), that variable amounts of entrainment was issuing from the exhaust line and an odor of $Cl_2$ was detectable from weak to strong in the proximity. Obviously, the demister located on top of the scrubber tower could not filter out the fine deoplets created by the $H_2O$ spray head. The entrainment was swept out of the tower part of which coalesced to form a liquid pool at the base of the gas line.

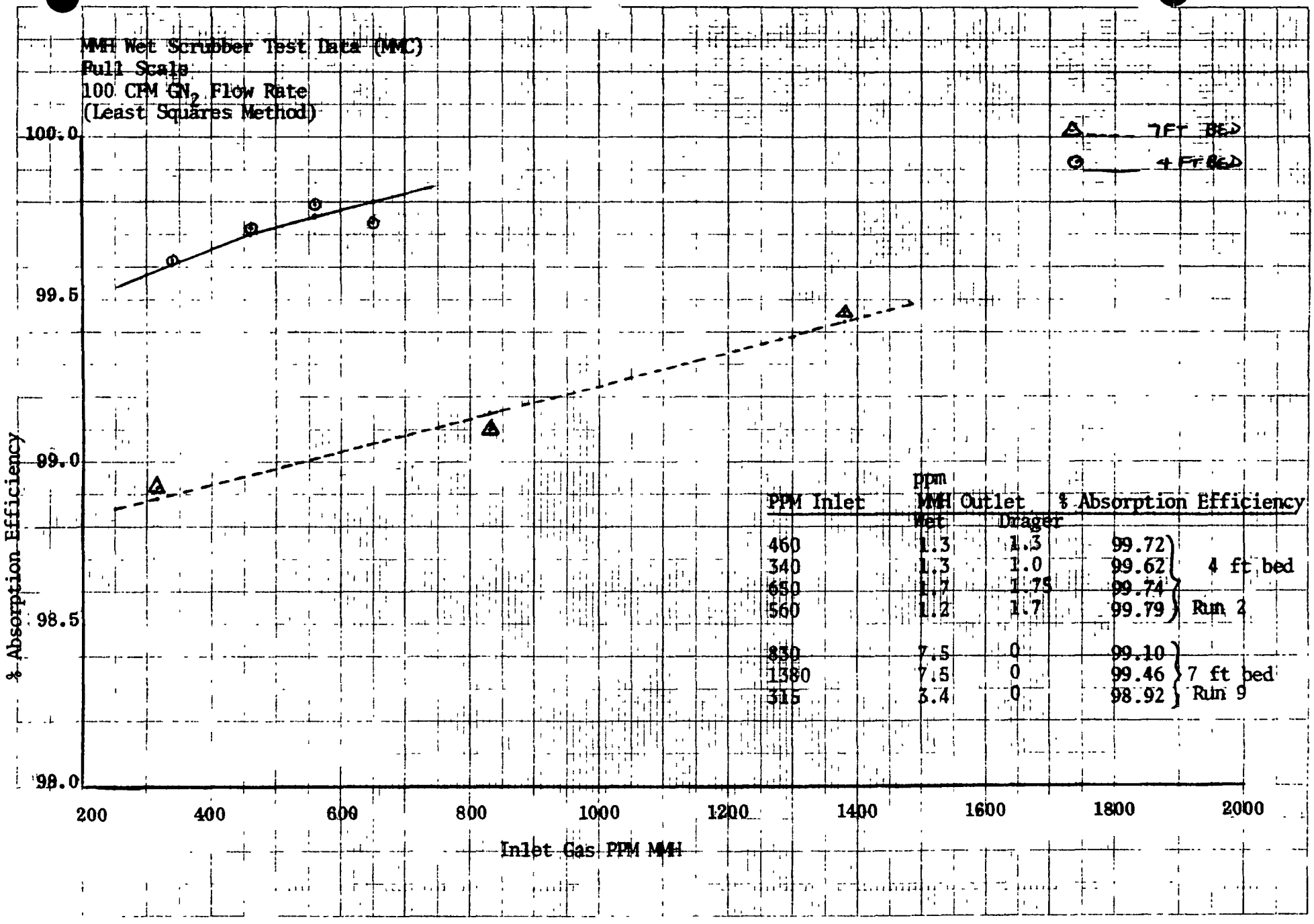
It is quite possible that some of this entrainment was drawn into the syringe during sample taking. $Cl_2$ interferes with the analytical method yielding high results, if present. This factor may account for the higher results shown in the wet method than those obtained with Drager readings. The entrainment problem did not arise during the F.I.T. scrubber experimental runs due to the low $GN_2$ flow rates.

FIGURE 23



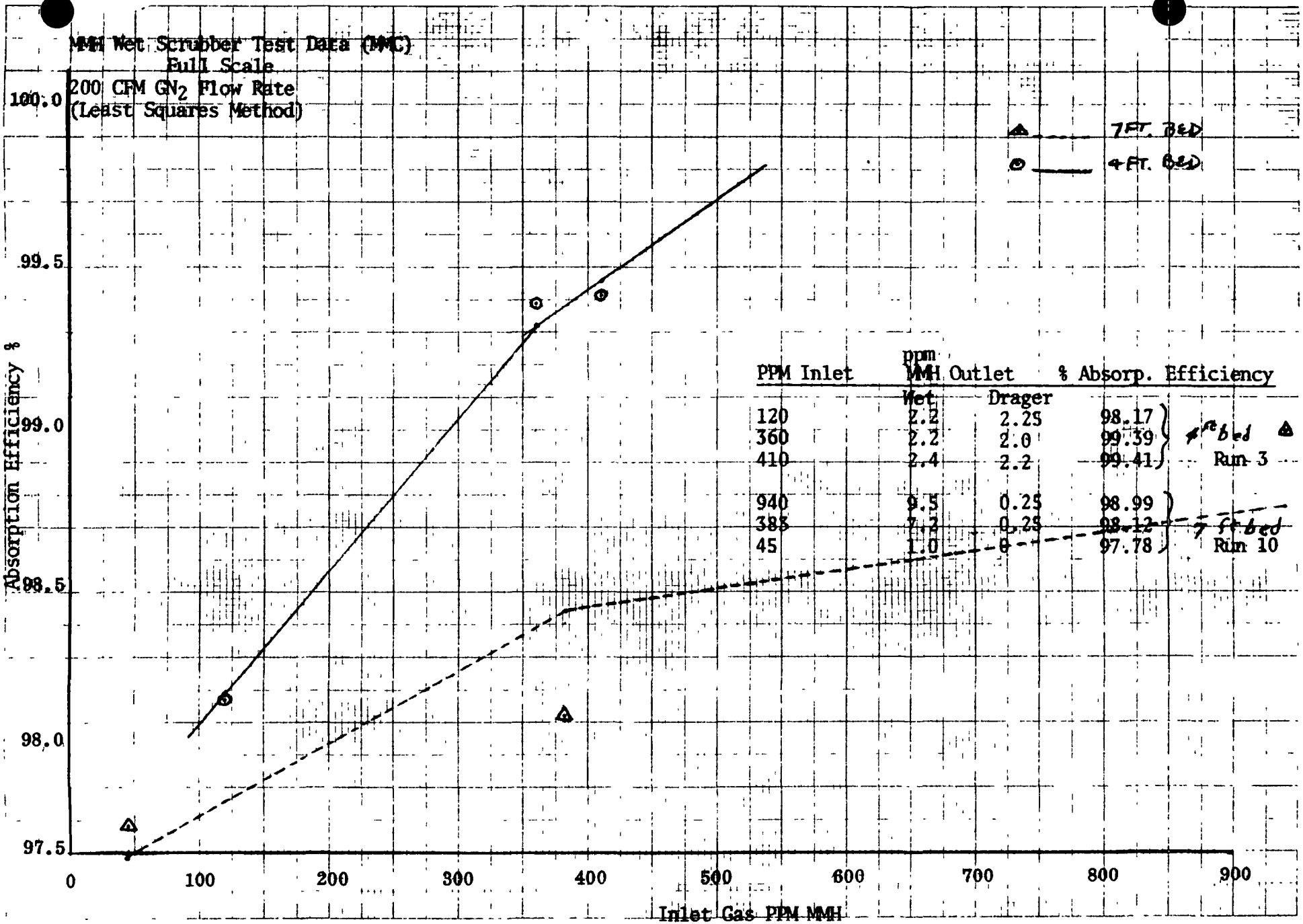

| Inlet ppm | ppm MMH Outlet Wet | Drager | % Absorption Eff | |
|---|---|---|---|---|
| 650 | 4.5 | 0 | 99.31 | |
| 620 | 4.0 | 0 | 99.35 | |
| 280 | 4.0 | - | 98.57 | 4 ft bed |
| 290 | 2.9 | - | 99.0 | Run 1 |
| 380 | 2.4 | 2.0 | 99.37 | |
| 250 | 5.0 | 0 | 98.00 | |
| 10,000 | 4.5 | 0 | 99.96 | 7 ft bed |
| 950 | 2.5 | 0 | 99.74 | |
| 330 | 1.7 | 0 | 99.48 | |
| 1360 | 1.0 | 0 | 99.93 | |
| 600 | 1.0 | 0 | 99.83 | Run 4,6,7, 8 |

FIGURE 24




| PPM Inlet | ppm MMH Outlet Wet | Drager | % Absorption Efficiency | |
|---|---|---|---|---|
| 460 | 1.3 | 1.3 | 99.72 | 4 ft bed Run 2 |
| 340 | 1.3 | 1.0 | 99.62 | |
| 650 | 1.7 | 1.75 | 99.74 | |
| 560 | 1.2 | 1.7 | 99.79 | |
| 850 | 7.5 | 0 | 99.10 | 7 ft bed Run 9 |
| 1380 | 7.5 | 0 | 99.46 | |
| 315 | 3.4 | 0 | 98.92 | |

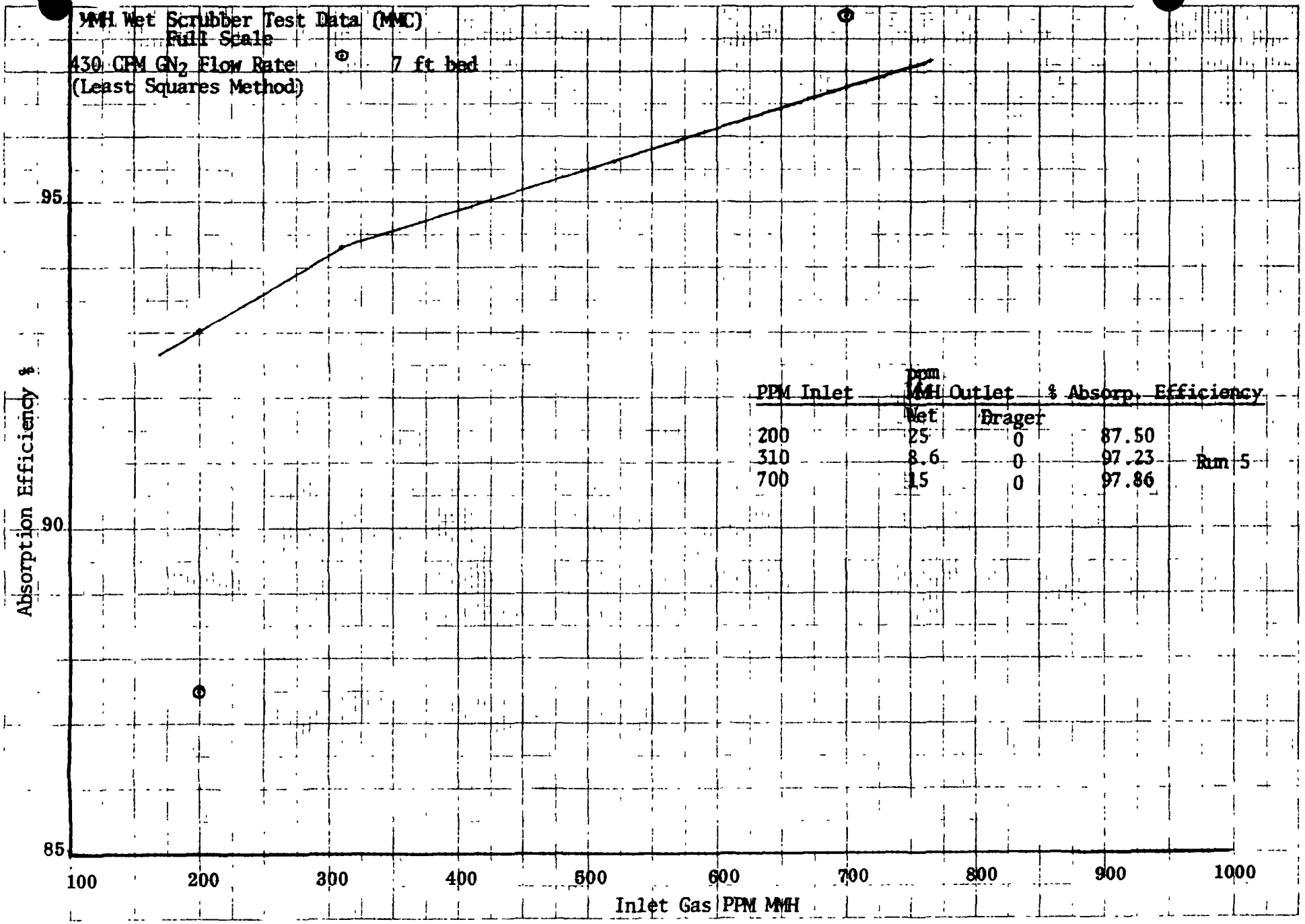
FIGURE 25




| PPM Inlet | ppm MMH Outlet Wet | Drager | % Absorp. Efficiency | |
|---|---|---|---|---|
| 120 | 2.2 | 2.25 | 98.17 | 4 ft bed Run 3 |
| 360 | 2.2 | 2.0 | 99.39 | |
| 410 | 2.4 | 2.2 | 99.41 | |
| 940 | 9.5 | 0.25 | 98.99 | 7 ft bed Run 10 |
| 385 | 7.2 | 0.25 | 98.12 | |
| 45 | 1.0 | 0 | 97.78 | |

06

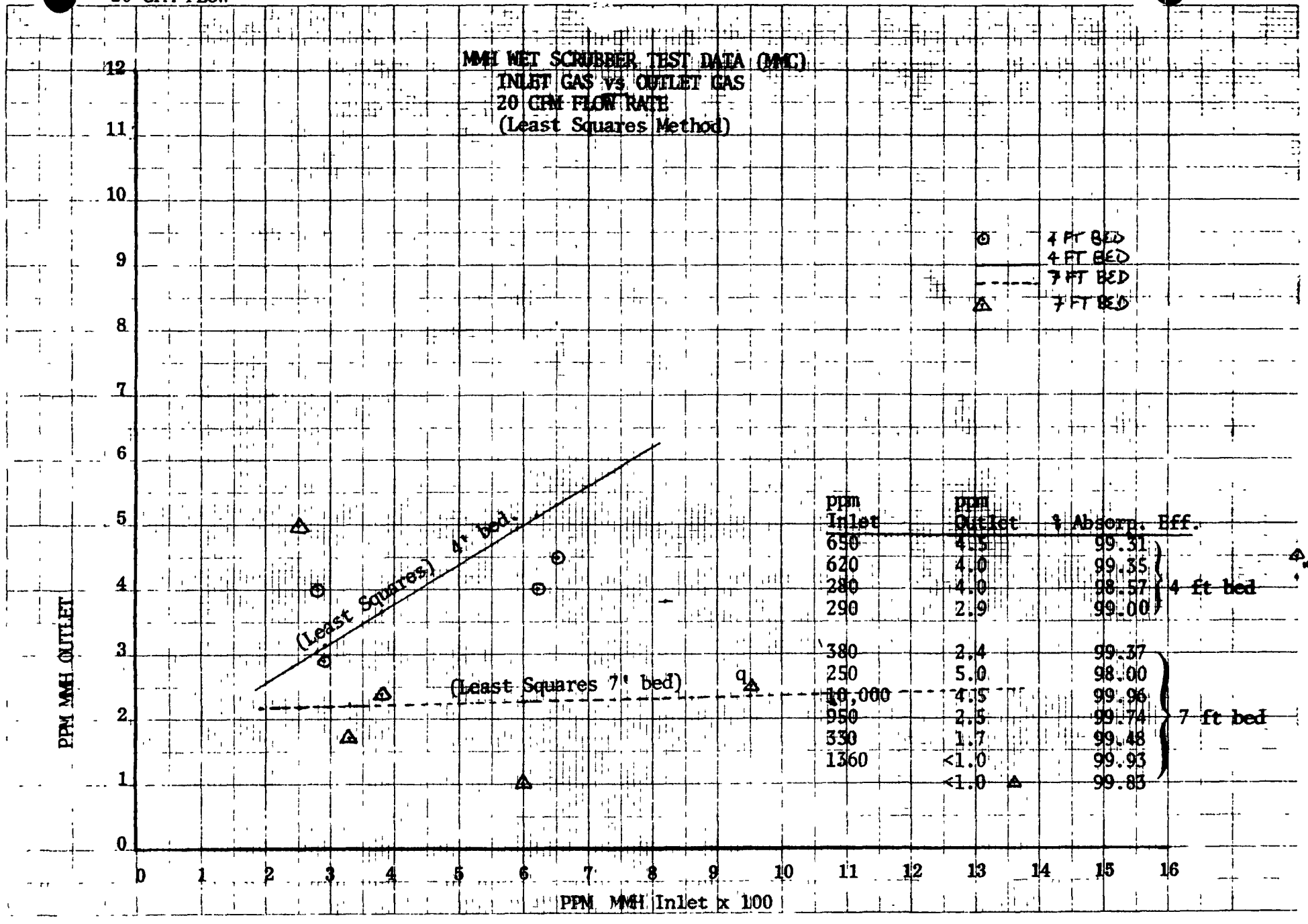
FIGURE 26




| PPM Inlet | ppm MMH Outlet | | % Absorp. Efficiency | |
|---|---|---|---|---|
| | Wet | Drager | | |
| 200 | 25 | 0 | 87.50 | |
| 310 | 8.6 | 0 | 97.23 | Run 5 |
| 700 | 15 | 0 | 97.86 | |

20 CFM FLOW

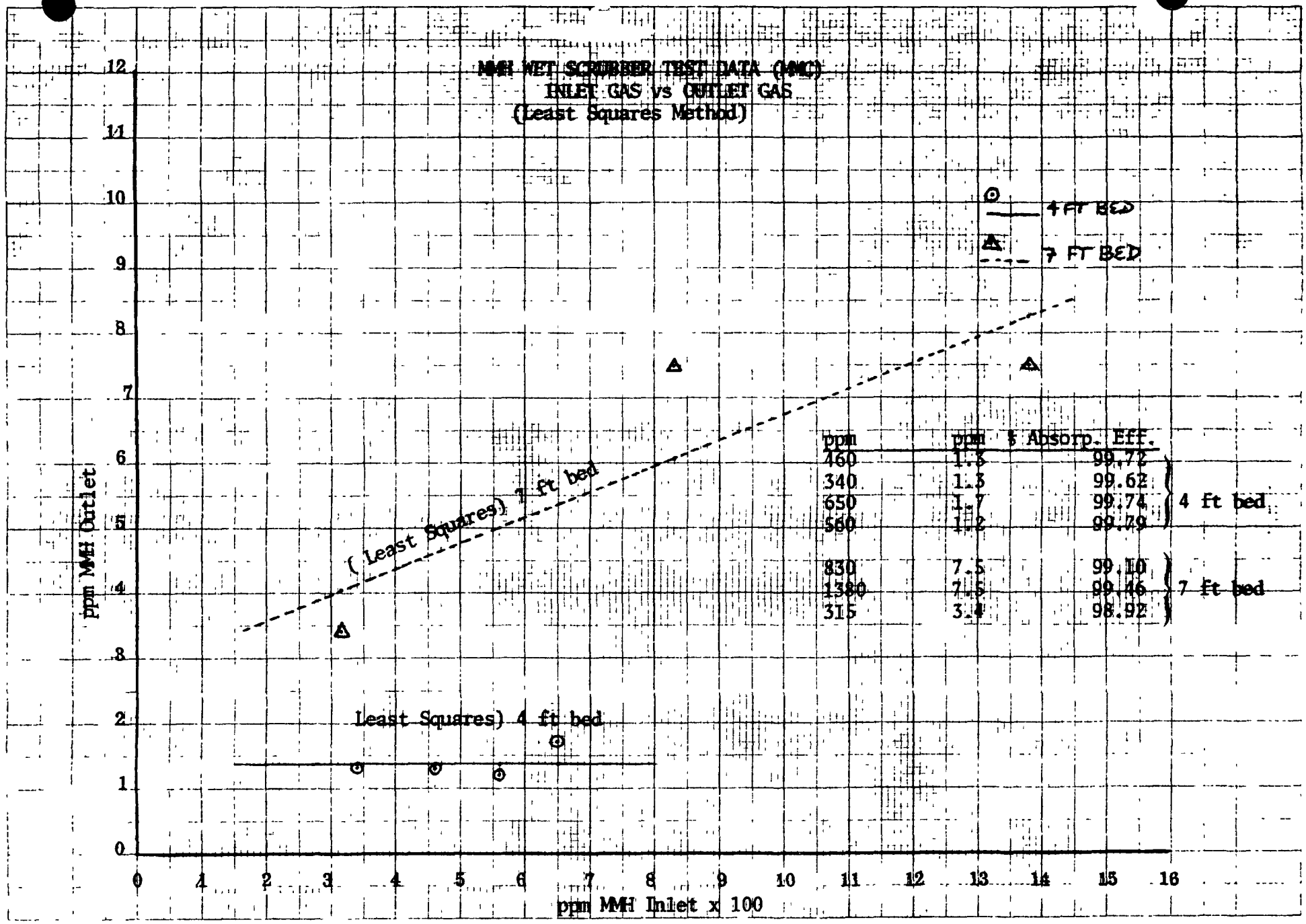
FIGURE 27


MMH WET SCRUBBER TEST DATA (MMC)
INLET GAS vs OUTLET GAS
20 CFM FLOW RATE
(Least Squares Method)
4 FT BED
4 FT BED
7 FT BED
7 FT BED
(Least Squares) 4' bed
(Least Squares 7' bed)
PPM MMH OUTLET
PPM MMH Inlet x 100
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
0 1 2 3 4 5 6 7 8 9 10 11 12

| ppm Inlet | ppm Outlet | % Absorp. Eff. | |
|---|---|---|---|
| 650 | 4.5 | 99.31 | 4 ft bed |
| 620 | 4.0 | 99.35 | |
| 280 | 4.0 | 98.57 | |
| 290 | 2.9 | 99.00 | |
| 380 | 2.4 | 99.37 | 7 ft bed |
| 250 | 5.0 | 98.00 | |
| 10,000 | 4.5 | 99.96 | |
| 950 | 2.5 | 99.74 | |
| 330 | 1.7 | 99.48 | |
| 1360 | <1.0 | 99.93 | |
| | <1.0 | 99.83 | |

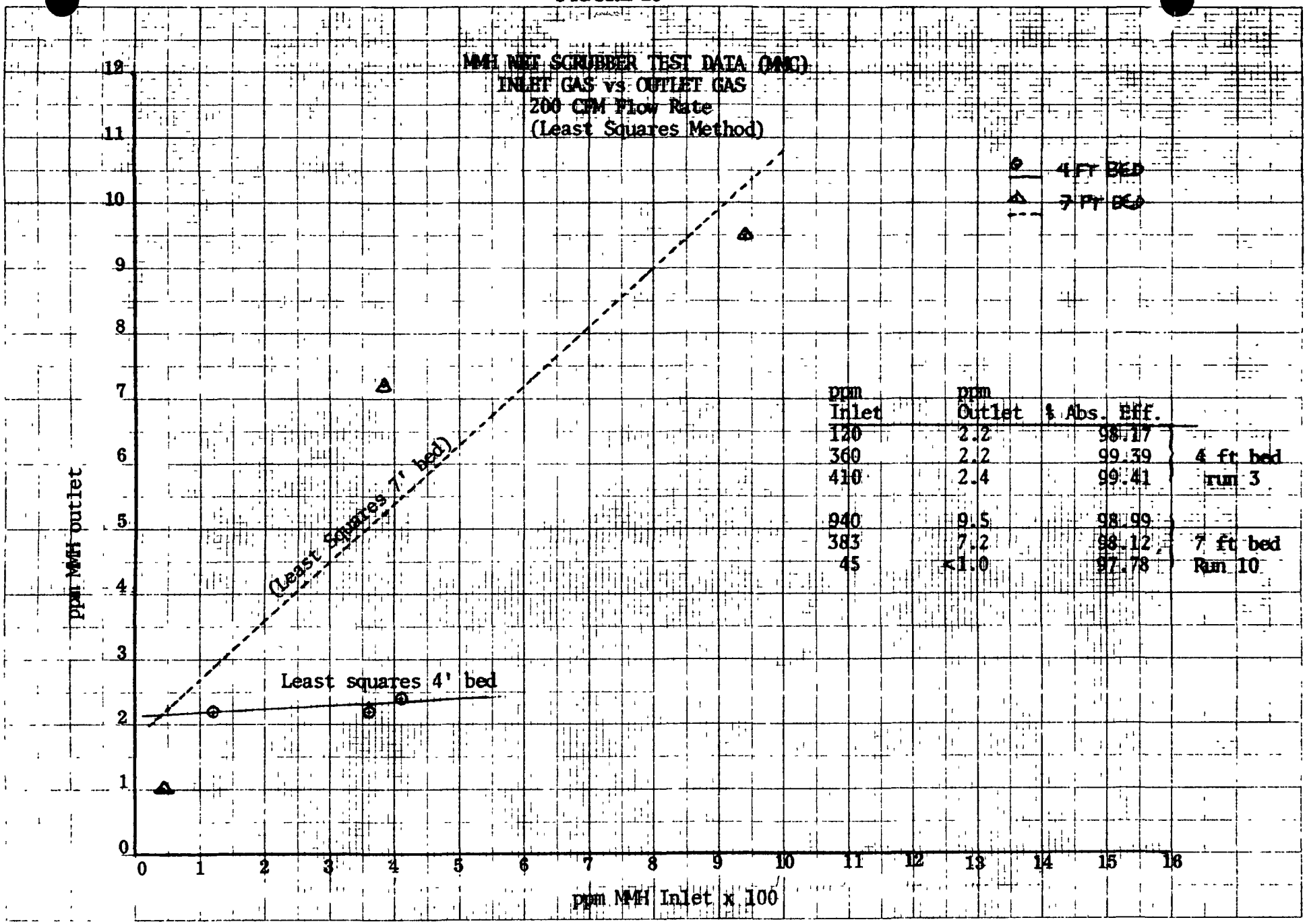
100 CFM FLOW

FIGURE 28




| ppm | ppm | % Absorp. Eff. | |
|---|---|---|---|
| 460 | 1.8 | 99.72 | 4 ft bed |
| 340 | 1.3 | 99.62 | |
| 650 | 1.7 | 99.74 | |
| 560 | 1.2 | 99.79 | |
| 830 | 7.5 | 99.10 | 7 ft bed |
| 1380 | 7.5 | 99.46 | |
| 315 | 3.4 | 98.92 | |

**FIGURE 29**




| ppm Inlet | ppm Outlet | % Abs. Eff. | |
|---|---|---|---|
| 120 | 2.2 | 98.17 | |
| 360 | 2.2 | 99.39 | 4 ft bed |
| 410 | 2.4 | 99.41 | run 3 |
| 940 | 9.5 | 98.99 | |
| 383 | 7.2 | 98.12 | 7 ft bed |
| 45 | <1.0 | 97.78 | Run 10 |

The entrainment problem is hardly a problem. It can be easily solved by providing a more suitable demister than the one used. The one used at MMC was of very course screening, about 7 x 7 inches square and 3/4" thick - hardly adequate to withhold anything but large drops of water.

Averaged Data

The MMC data for each flow rate was lumped together and then averaged with results appearing in Table 17, below.

TABLE 17

AVERAGED MMC DATA FOR MMH SCRUBBER RUNS

| $GN_2$ FLOW RATE CFM | % ABSORPTION EFFIC. BASED ON WET ANALYSIS | RANGE MMH IN EFFLUENT GAS PPM | % ABSORPTION EFFIC. BASED ON DRAGER READINGS | RANGE MMH IN EFFLUENT PPM INDICATED |
|---|---|---|---|---|
| 20 | 99.5 | <1.0-7.5 | 99.5-100 | 0-2.0 |
| 100 | 99.3 | 1.2 - 7.5 | 99.6 - 100 | 0 - 1.75 |
| 200 | 98.6 | 1 - 9.5 | 99.4 - 100 | 0 - 2.25 |
| 430 | 94.2 | 8.6 - 25 | 100 | 0 |

It is seen that absorption efficiencies are excellent when based on Drager readings but fall off with increased $GN_2$ flow rate when based on wet analysis.

Water Flow Rate Optimization

Three weeks testing time was used up in making trial runs and equipment modifications, allowing insufficient time to perform additional tests. One scheduled test omitted was to optimize the recirculating water flow rates for the different

$GN_2$ flow rates. A constant 20 $\pm$ .4 GPM rate was used throughout the program.

Saddles

Three-quarter inch Raschig rings or intalox saddles were specified for the scrubber packing. However, one inch by 1/2 inch saddles were received with no opportunity to exchange due to the time limit. It is believed that use of the larger packing with larger voids decreased the non-critical $\Delta P$ but also decreased absorption efficiency by the reduced surface area, which was critical.

Scrubber Liquor Analysis

The progress of NaOCl scrubber bath exhaustion was followed by periodic analysis for percent residual $Cl_2$. Two charges of this bath were used during the three days testing period. The first charge consisted of approximately 200 gallons of 3% solution introduced into the storage tank. An unknown part of this charge leaked out during the night through a cracked valve. Four runs were made before the bath was exhausted and dumped. A second fresh charge of about 300 gallons of 5.09% $Cl_2$ solution was then made up and the remaining six test runs completed. The final solution contained 0.71% residual $Cl_2$. In all about 55-60 lbs. of liquid MMH was fed into the scrubber during the ten runs. A rough calculation shows the dry weight equivalent of the two charges to be about 180 lbs. NaOCl. Thus, about 3.3 lbs. NaOCl were required for each pound MMH destroyed.

## 8. VOLATILE PRODUCTS OF THE MMH, NaOCl SCRUBBING REACTION

Data obtained from crypgenically trapped effluent from the trial run at MMC conducted 8-17-76 using the four-foot bed.

Total number of peaks observed in the g.l.c. is 14, of which 7 seem significant, and 5 are identified. The pertinent data are listed in Table 18.

TABLE 18

Volatile Products of the MMH, NaOCl Scrubbing Reaction

| g.l.c. Retention Time Minutes | Reaction Product | Approximate Concent. ppm | Carcinogenicity* | 1974 USOS air TWA ppm |
|---|---|---|---|---|
| 0.68 | $CH_3Cl$ | 115.0 | NT | 100 |
| 1.80 | $CH_3OH$ | 19.6 | NCA | 200 |
| 2.90 | $CH_2Cl_2$ | 30.9 | NCA | 500 |
| 4.10 | $CH_3NHNH_2$ | 4.6 | CA | 350 ug/$M_3$ ceiling conc. |
| 5.90 | $CHCl_3$ | 1.2 | CA | 50 |
| 6.30 | $CCl_4$ | undetected | CA | 10 |

* NT - Not tested
NCA = Non carcinogenic
CA = carcinogenic

Mass spec data shows peaks at the dalton numbers shown in Table 19. Likely candidates which correspond to these values and their approximate concentrations are also shown. No peaks were obtained higher than 53.5.

TABLE 19

| Dalton No. | Molecule or Atom | Concentration |
|---|---|---|
| 32 | $CH_3OH$ | 10-200 ppm |
| 35 | Cl | 10-200 ppm |
| 37 | Cl | 10-200 ppm |
| 51.5 | $CH_3Cl$ | 10-200 ppm |
| 53.5 | $CH_3Cl$ | 10-200 ppm |

## 9. CONCLUSIONS

Based on the above results, the following conclusions were drawn:

1. The MMH scrubber successfully demonstrated a capability to sufficiently reduce the MMH concentration to less than 10 ppm at full flow variable purge rates of 20 to 430 CFM and variable input MMH concentrations of 45 to 10,000 ppm.

2. Drager tube readings showed 0 ppm in about half the cases and a maximum of 2.25 ppm in the worst case. But wet analysis showed higher MMH concentrations possibly as a result of $Cl_2$ interferences, due to the entrainment problem.

3. The seven-foot bed showed higher absorption efficiencies than the four-foot bed when based on Drager readings.

4. The MMC results on the large scrubber approximately parallel the F.I.T. results on the small unit as far as percent absorption efficiency and effluent concentrations are concerned.

# CHAPTER 4

# THE LOW FLOW PACKED BED ABSORPTION EXPERIMENTS USING OTHER SCRUBBING AGENTS

## 1. $NH_4OH$ WET SCRUBBING SYSTEM FOR $N_2O_4$

A reinvestigation of dilute $NH_4OH$ as a scrubbing liquor was deemed advisable after conferences with representatives of Heat Systems Ultrasonics, a scrubber manufacturer. They advised the use of $NH_3$ or NaOCl in our particular scrubbing system for $N_2O_4$. After examining our previous results with $NH_4OH$, it was determined that the initial unattractive results could have been caused by the presence of a white cloud of $NH_4NO_3$ in the effluent which would give the same positive results as $NO_2$ in the wet chemistry analytical procedure utilized. Also, a dry scrubber was envisioned as being much more efficient for $NH_4NO_3$ and $NH_3$ than for $NO_2$. Therefore, the runs in Figures 30 through 35 were conducted. The pertinent data are included on the figures. The dry scrubber was used in this and in subsequent experiments. The composition and theory of the dry scrubber is discussed in the Task 8 Report.

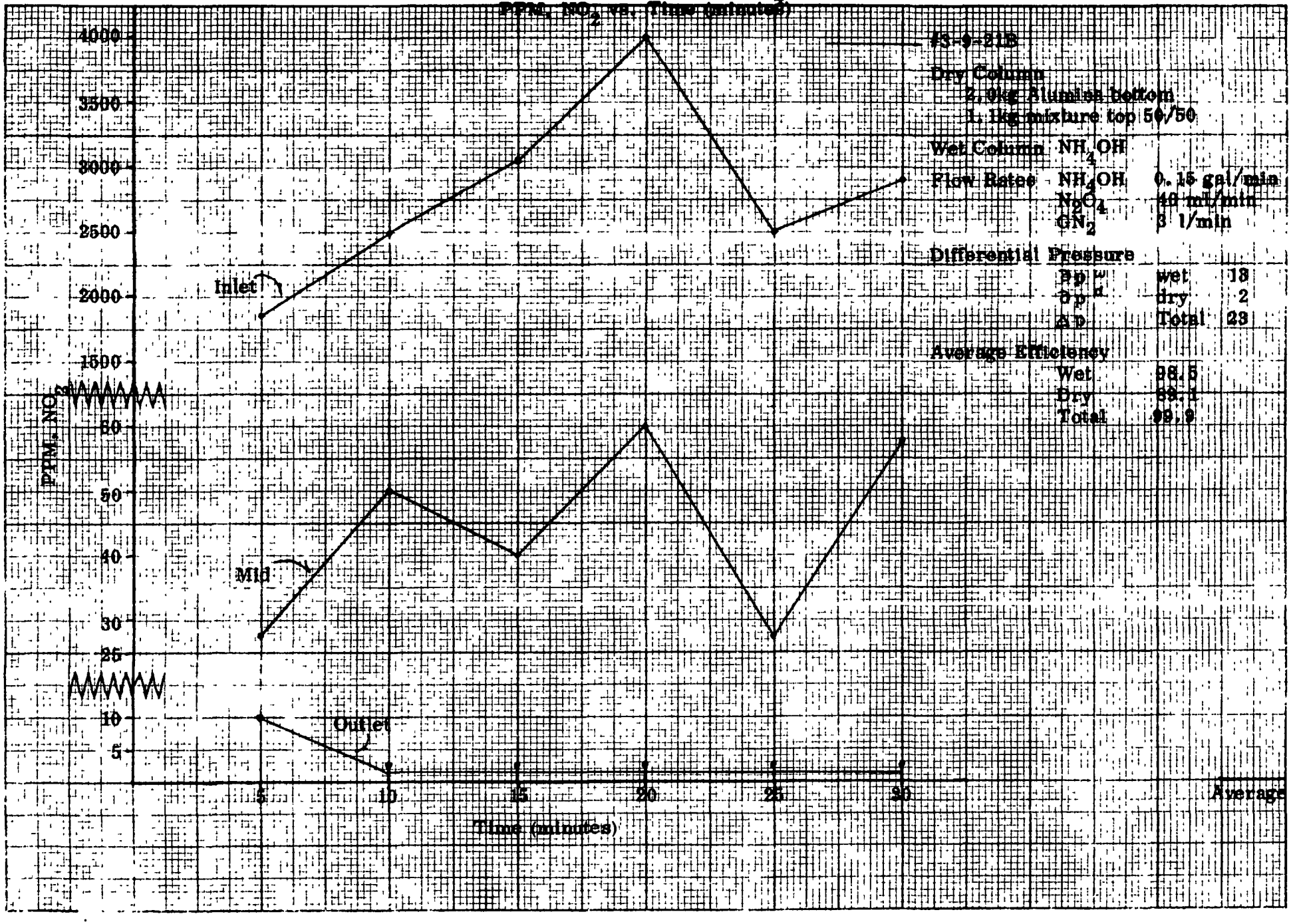
Essentially, the $NH_4OH$ system worked in the manner expected with extremely low output of $NO_2$ from the dry scrubber ("out" ppm $NO_2$).

The one disadvantage of the $NH_4OH$ system is an evident effluent of $NH_3$ and $NH_4NO_3$.

The advantages of the $NH_4OH$ system are as follows:

1. $NH_4NO_3$ or $NH_3$ effluents are not carcinogenic.
2. $NH_4NO_3$ in the scrubbing liquor can be disposed of simply by heating the solution to boiling. $N_2O$ nitrous oxide, forms which is not a pollutant. The remaining water can then be disposed of in a sewer stream.
3. Extremely low effluents of $NO_2$ are obtained.
4. All the relevant chemistry is known.

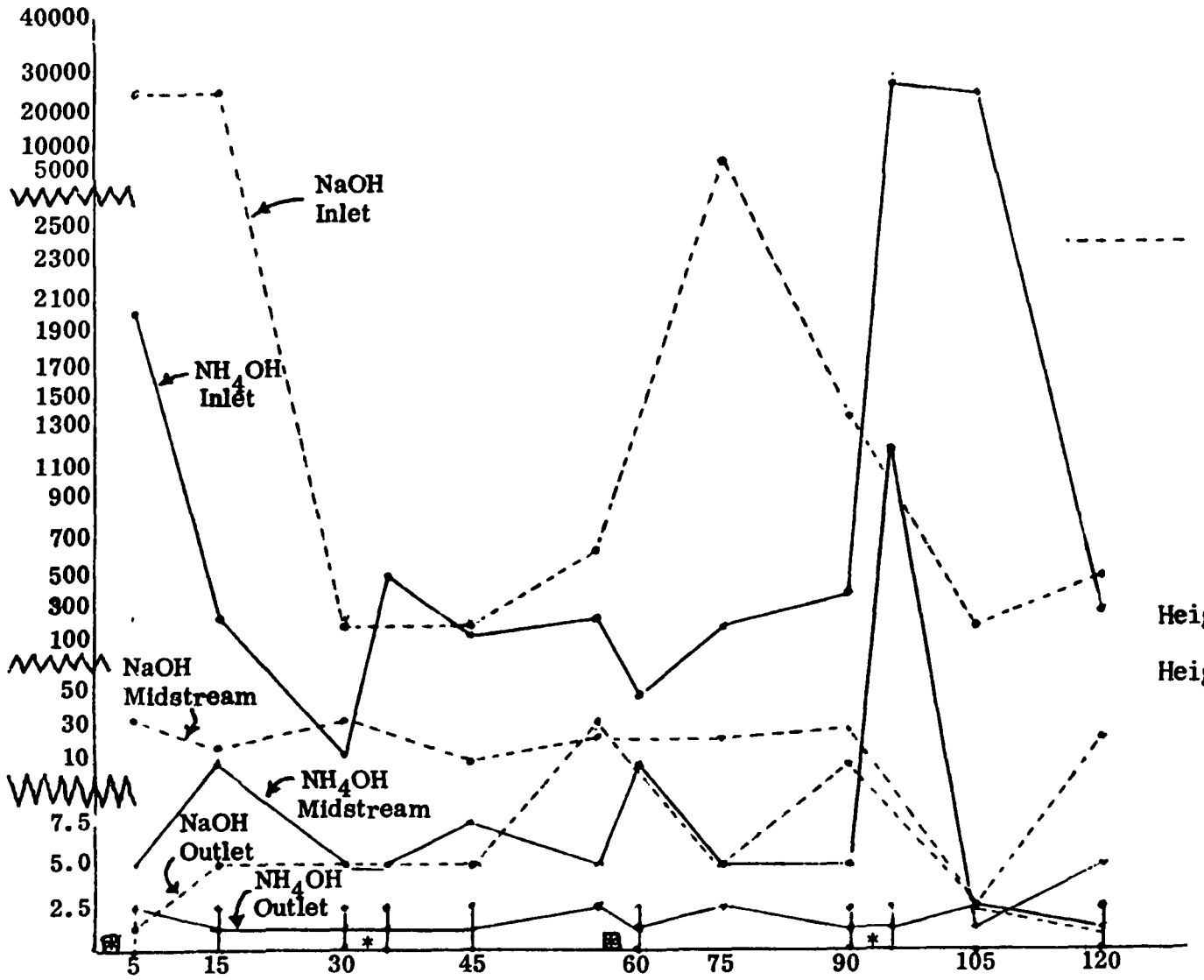
Combination Wet-Dry Scrubber System Utilizing $NH_4OH$ as Wet Scrubber Solution




11/5/76

FIGURE 30

Combination Wet-Dry Scrubber #3-9-22A System, Comparison of $NH_4OH$ to NaOH PPM, $NO_2$ vs. Time (minutes)




$NH_4OH$ Solution #3-9-22A
$GN_2$ Flow 3 liters/min
Solution Flow 0.15 gal/min
$N_2O_4$ Flow varied

Differential Pressure
$\partial P^{w}$ wet 13.0"
$\partial P^{d}$ dry 2.0"
$\Delta P$ total 23.0"

NaOH Solution #3-9-27A
$GN_2$ Flow 3 liters/min
Solution Flow 0.15 gal/min
$N_2O_4$ Flow varied

Sample taken:
Inlet - between the gas mixing column and the wet scrubber.

Midstream - between the wet scrubber and the dry scrubber.

Exit - After dry scrubber

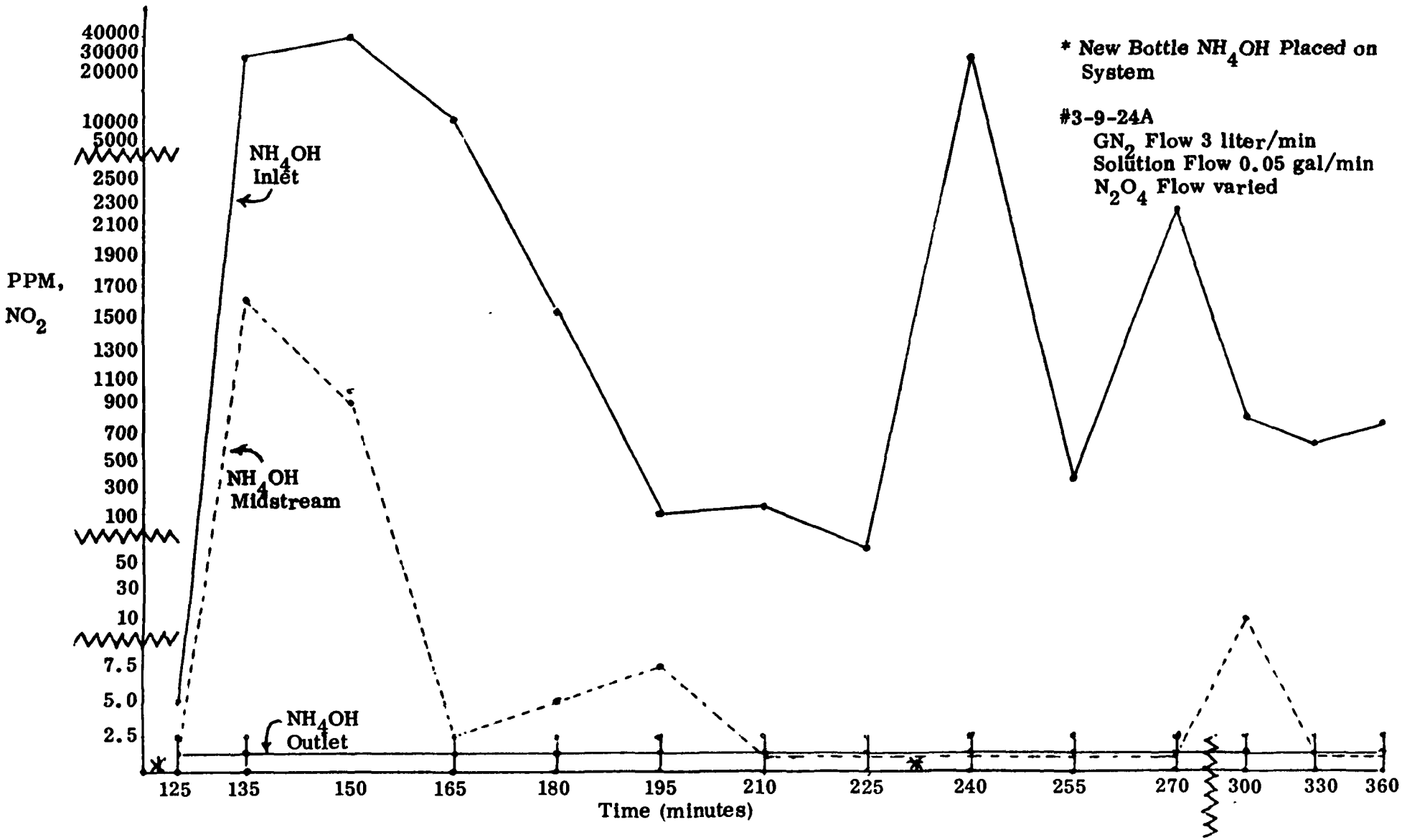
Dry Column
Height 30 cm bottom 2.0 kg
100% Alumina
Height 30 cm top 1.2 kg
50% Alumina to
50% Charcoal



9/28/76

Figure 31

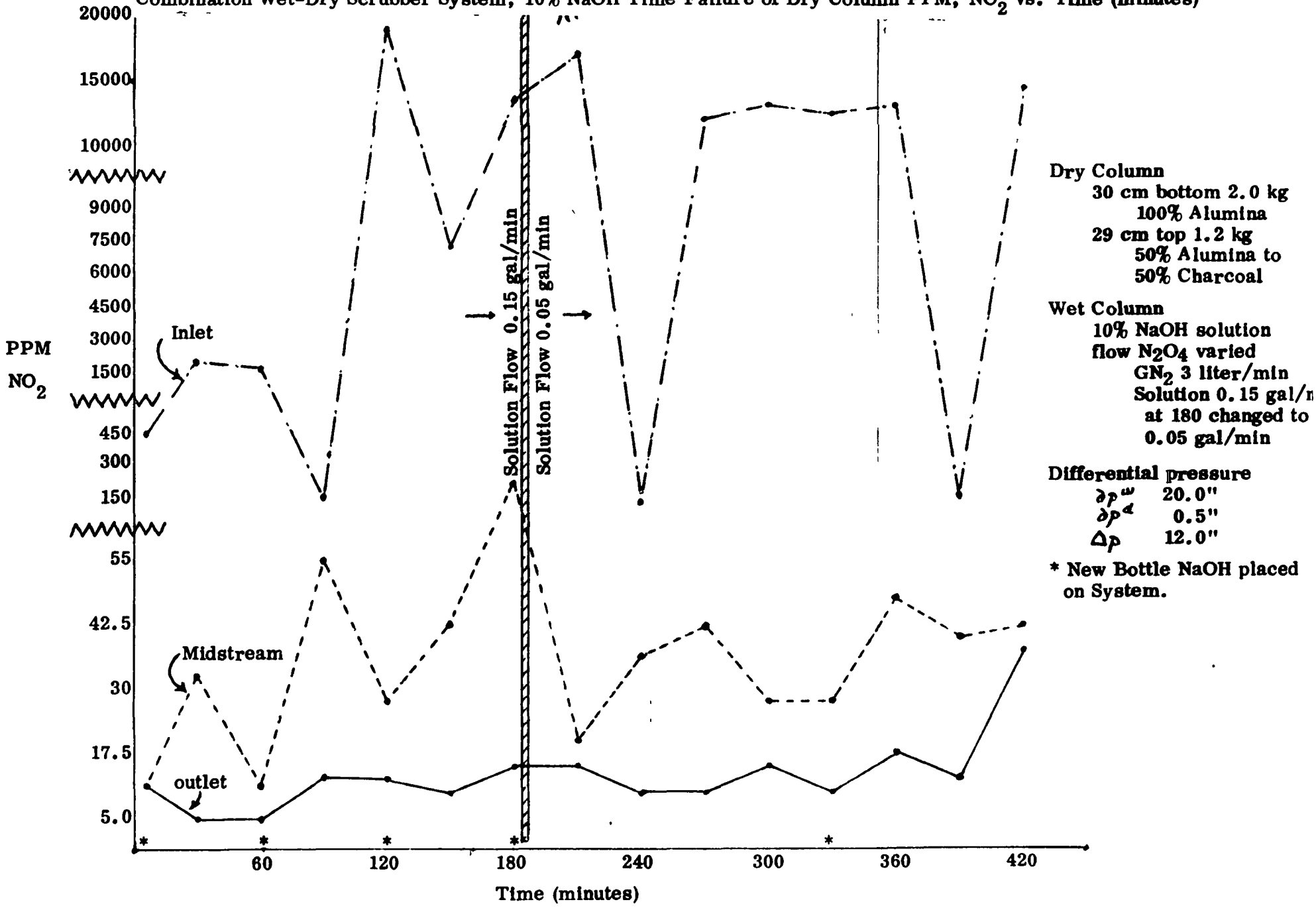
Continuation $NH_4OH$ Wet-Dry Scrubber #3-9-24A, PPM, $NO_2$ vs. Time (minutes)






9/28/76 BC

Figure 32

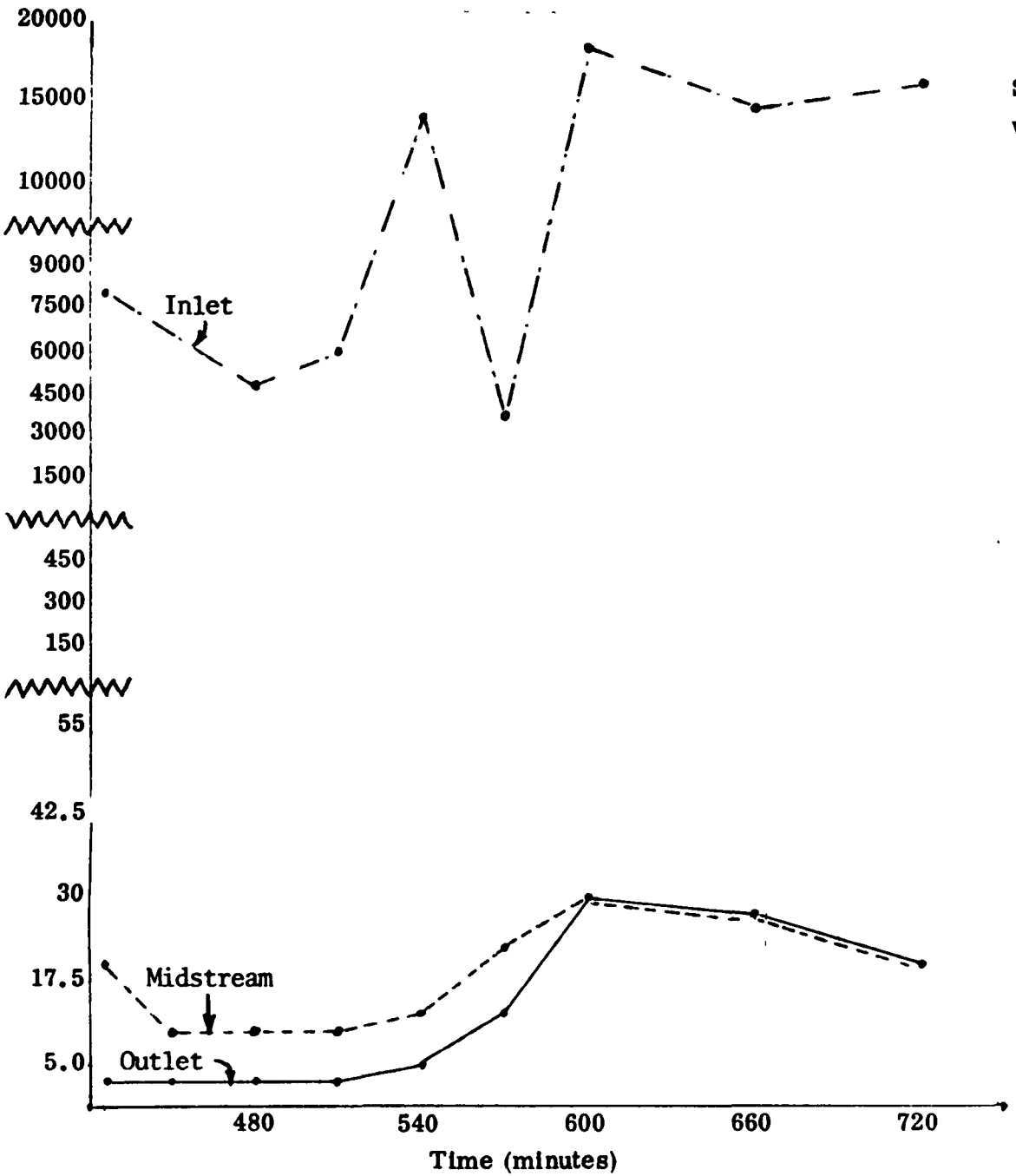





10/5/76

Figure 33

Combination Wet-Dry Scrubber System, 10% NaOH T\ ₃ Failure of Dry Column PPM, $NO_2$ vs. Time (minute\




Same Parameters as 180 through 420 minutes.

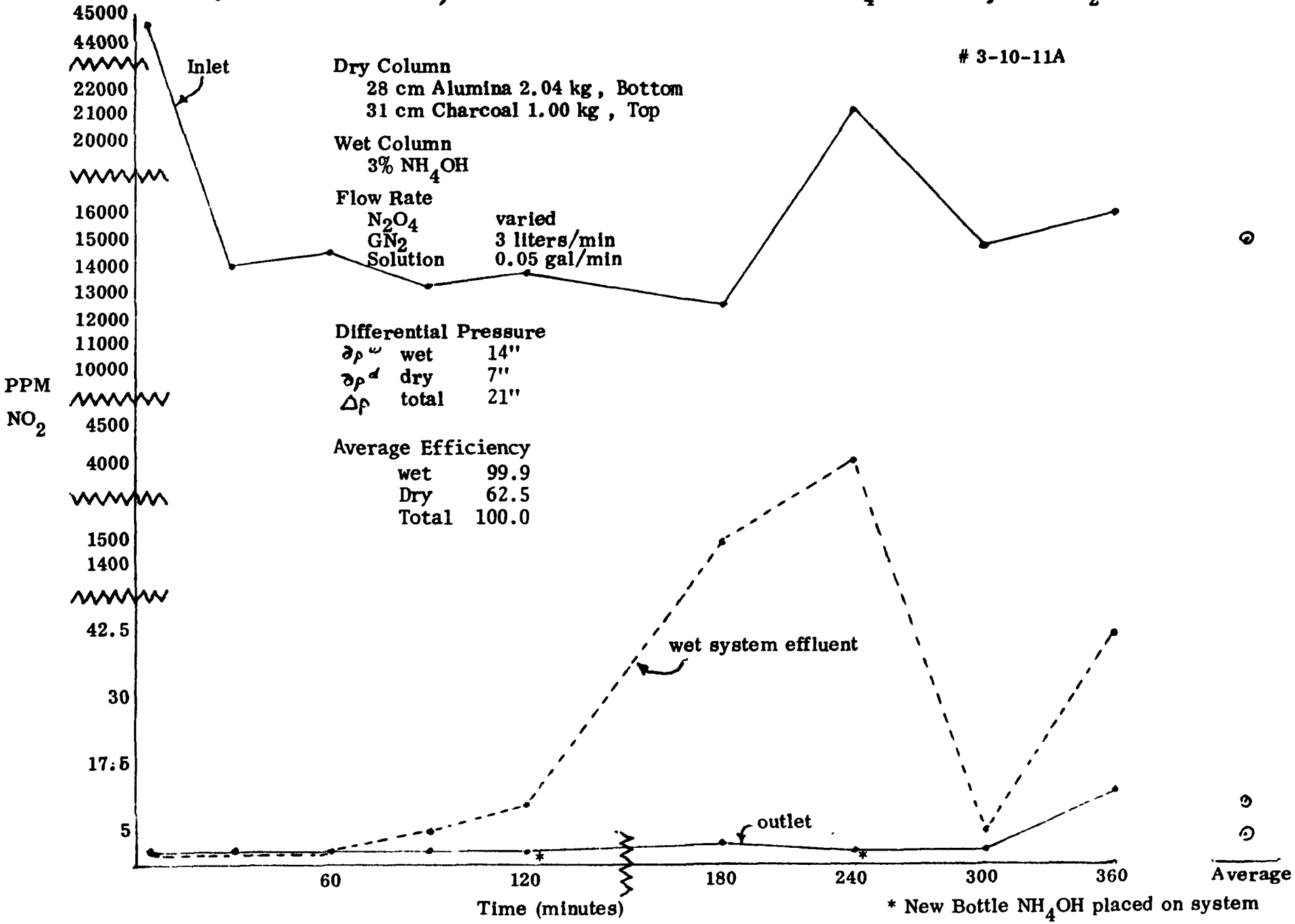
Weight Charges:
$N_2O_4$ -0.216 lbs (-0.09 kg)
Alumina 0.0

105

10/5/76

Figure .34

Co...bination Wet-Dry Scrubber ... System, Time Failure of ...y Column using 10% $NH_4OH$ Solution, PPM, $NO_2$ vs. Time (minutes)




10/13/76 BC

Figure 35

## 2. NaOCl WET SCRUBBING SYSTEM FOR $N_2O_4$

NO is a very insoluble species formed when $N_2O_4$ dissolves in water. However, it readily reacts with $Cl_2$ to form nitrosyl chloride NOCl which reacts with water to form nitrous oxide, $N_2O$, a non-polluting stable species. Therefore, the use of NaOCl, a source of $Cl_2$, was investigated as a scrubber liquor additive. The results are shown in Figures 36 and 37. As is seen, the wet scrubbing efficiency is very high.

### Advantages

1. The wet scrubbing efficiency is very high.

### Disadvantages

1. The NOCl formed is sickening.
2. The dry scrubber stage is not very effective.

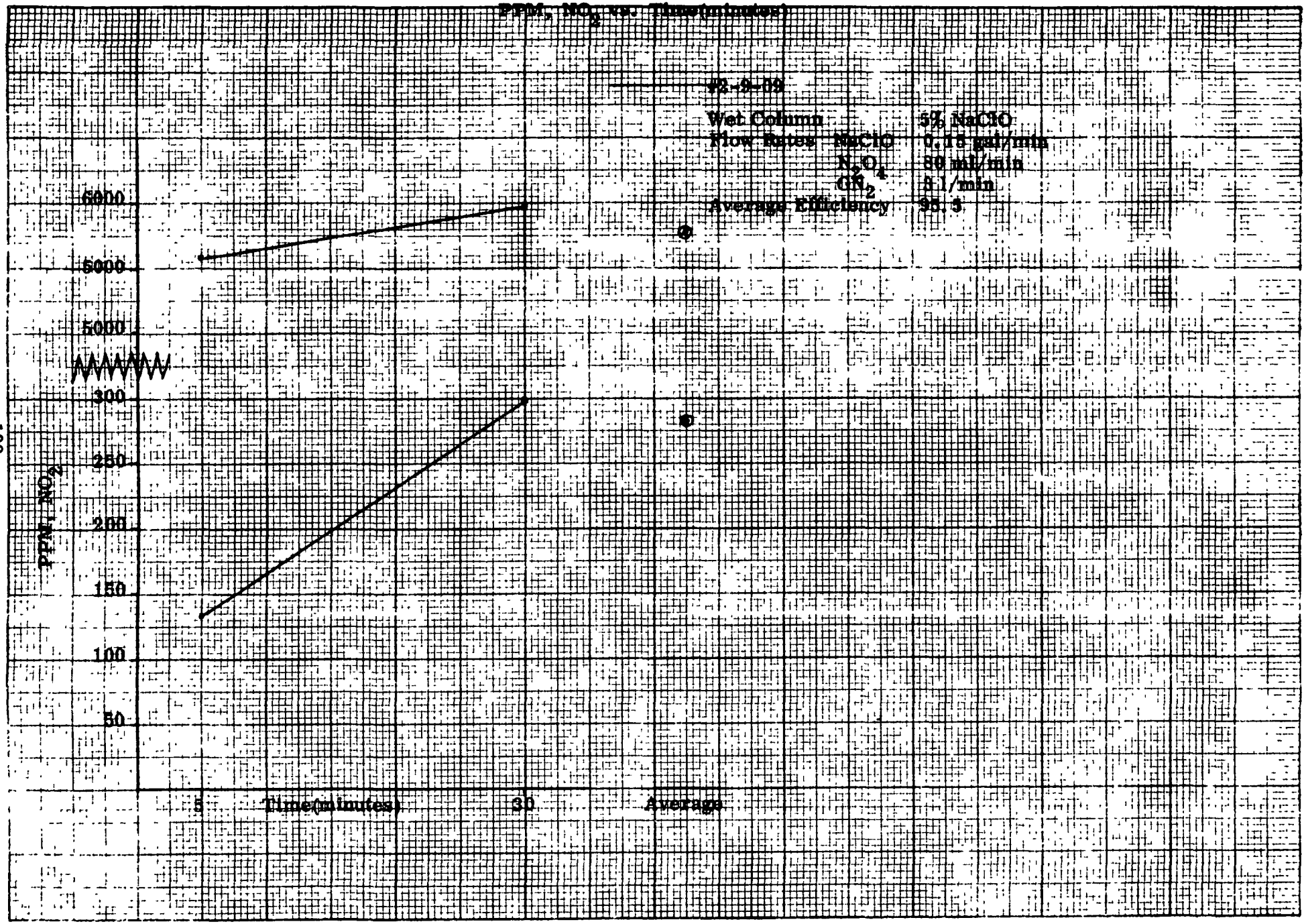
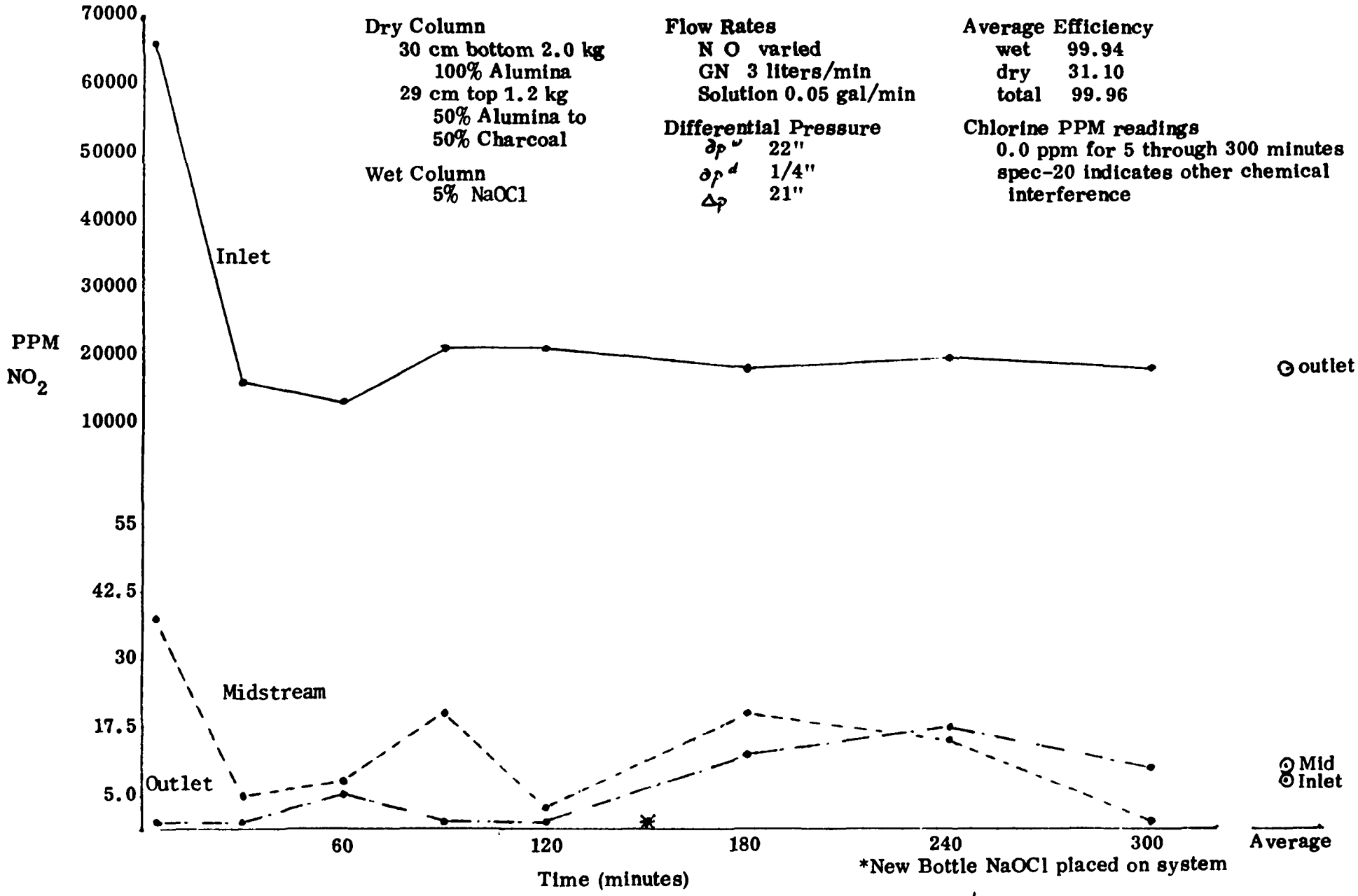

Wet Scrubber System Utilizing 5% NaOCl Solution
PPM, $NO_2$ vs. Time(minutes)
#2-19-69
Wet Column
Flow Rates NaClO
$N_2O_4$
$GN_2$
Average Efficiency
5% NaClO
0.15 gal/min
80 ml/min
8 l/min
95.5
6000
5000
5000
300
250
200
150
100
50
PPM $NO_2$
5
Time(minutes)
30
Average

FIGURE 36

Combination Wet-Dry Scrubber 22A System, Time Failure of Dry Column using 5% NaOCl Solution, PPM, $NO_2$ vs. Time (minutes)

#3-10-07A




10/11/76 BC

Figure 37

## 3. TRIETHANOLAMINE

In an effort to improve the absorption efficiency in wet scrubbing of $N_2O_4$ vapors from gas streams a literature search was undertaken to find a suitable substitute for NaOH solution. Several potential reagents were selected. One of the most promising was triethanolamine, among others.

A series of six runs was made with the existing F.I.T. laboratory model wet scrubber. The operating conditions were identical to those used for the NaOH runs except a 3% solution of TEA was substituted. Surprisingly excellent results were obtained. Table 20 summarizes these results. With inputs of approximately 550 to 9,750 ppm $N_2O_4$ outputs averaged from 2.9 to 5.8 ppm $NO_x$ and absorption efficiencies averaged 99.75%. In comparison with results from NaOH runs, these are much better. Specifically, 18 effluents analyzed were found to be in a range of 1.3 to 11 ppm $NO_x$ which is about 1/10 of those from NaOH runs. (See Table 9) At such low toxic effluents and second stage scrubber would not be necessary.

However, a dry tower was connected to the exit line from the wet scrubber. The dry tower was partly filled with $Al_2O_3$, as desiccant, and partly with activated carbon, as adsorbent. Samples were taken at the influent line to the wet scrubber and exit lines from both wet and dry towers. These results appear in Table 21. Again, results were excellent.

In five out of six cases complete adsorption (100%) of $NO_x$ occurred. In the sixth case, the effluent contained a mere 1.3 ppm $NO_x$ from an input of 14,500 ppm $N_2O_4$ - the adsorption efficiency being 99.993% for the two-staged system. Efficiencies like this would permit use of considerably smaller second stage scrubber than would be feasible with the NaOH solution (if it was mandatory to use a second stage).

TABLE 20

Results of Wet Scrubbing with 3% TEA
Single Stage F.I.T. Lab set-up)

| Run # | $N_2O_4$ Influent ppm | $N_2O_4$ Effluent ppm (avg. 3 anal) | % Absorpt. Efficiency | Comments |
|---|---|---|---|---|
| 1 | 5504 | 5.8 | 99.89 | Drager = 0 ppm |
| 2 | 4179 | 6.0 | 99.85 | Drager = 0 ppm |
| 3 | 1625 | 2.9 | 99.82 | |
| 4 | 8600 | 2.6 | 99.97 | |
| 5 | 557 | 5.3 | 99.04 | |
| 6 | 9750 | 3.3 | 99.96 | |
| | Average | 4.3 | 99.75 | |

TABLE 21

Results of Double Stage
(TEA in first wet stage and Act. Carbon in second stage)

| Run # | $N_2O_4$ Infl ppm | Eff fm wet Stage Nox ppm | Outlet fm dry stage $NO_x$ ppm | % Effic. Wet Stage | System Eff % | Comments |
|---|---|---|---|---|---|---|
| 7 | 330 | 25 | 0 | 92.42 | 100 | .06 GPM $H_2O$ flow |
| 8 | 14,500 | 238 | 1.3 | 98.36 | 99.993 | |
| 9 | 2225 | 0.75 | 0 | 99.96 | 100 | 20 GPM $H_2O$ flow |
| 10 | 6575 | 7.0 | 0 | 99.89 | 100 | |
| 11 | 7750 | 7.0 | 0 | 99.90 | 100 | |
| 12 | 3950 | 4.3 | 0 | 99.89 | 100 | |

Total Flow Rate ($N_2$ + $N_2O_4$) = 3 liters/min (all runs)

## Discussion

The results obtained with TEA are very encouraging from the standpoints of high absorption efficiency and low toxic gas levels in the effluent. Further work is projected with the objectives:

1. To thoroughly investigate the suitability of TEA for use in wet scrubbing as a substitute for NaOH
2. To discover possible limitations, if any.

It is too early to recommend use of TEA now, in lieu of NaOH, but it is strongly recommended to proceed immediately with the evaluation of TEA.

## Conclusions

Based upon the preliminary results, it was concluded that:

1. A 3% TEA solution is more absorbant than a 5% NaOH solution in a wet scrubber for removing $N_2O_4$ vapors from $N_2$ gas streams.
2. A single stage scrubber demonstrated an absorption efficiency of 99.7% with an extremely small $NO_x$ effluent. Coupled with a second dry stage, the system demonstrated essentially 100% efficiency.
3. Further work is adviseable to establish the advantages and disadvantages of TEA as a suitable material for use in wet scrubbers.

## Chemistry of the Reaction

The chemistry* involved in the reaction of $N_2O_4$ or $NO_x$ with triethanolamine are as follows:

1. $N_2O_4 + (C_2H_4OH)_3 \longrightarrow (C_2H_4OH)_3\,NHNO_3 + (C_2H_4OH)_3\,NHNO_2$

TEA

*Ref. "Chemical Cleaning of Titan II Engineers", J.J. Bost and R.E. Bernard Aerojet - General Corp., Sacramento, California.

2. $HNO_3 + (C_2H_4OH)_3N \longrightarrow (C_2H_4OH)_3 NH^+ NO_3^-$

Nitric Acid — Triethanolamine Hydrogen Nitrate

3. $HNO_2 + (C_2H_4OH)_3N \longrightarrow (C_2H_4OH)_3 NH^+ NO_2^-$

Nitrous Acid — Triethanolamine Hydrogen Nitrate

The reaction products are all very soluble in water.

Table 20

Results of Wet Scrubbing with 3% TEA (single stage)

(F. I. T. Lab Set-up)

| Run # | $N_2O_4$ Influent ppm | $N_2O_4$ Effluent ppm | % Absorption Efficiency | Comments |
|---|---|---|---|---|
| | | (Avg of 3 anal) | | |
| 1 | 5504 | 5.8 | 99.89 | Drager=0ppm |
| 2 | 4179 | 6.0 | 99.85 | Drager=0ppm |
| 3 | 1625 | 2.9 | 99.82 | |
| 4 | 8600 | 2.6 | 99.97 | |
| 5 | 557 | 5.3 | 99.04 | |
| 6 | 9750 | 3.3 | 99.96 | |
| | Average | 4.3 | 99.75 | |

Table 21

Results of Double Stage

(TEA in first wet stage and ACT Carbon in second Stage)

| Run # | $N_2O_4$ influent ppm | effluent from wet stage $NO_x$ ppm | outlet from dry Stage $NO_x$ ppm | % Efficiency Wet Stage | System Efficiency % | Comments |
|---|---|---|---|---|---|---|
| 7 | 330 | 25 | 0 | 92.42 | 100 | .05 GPM $H_2O$ flow |
| 8 | 14,500 | 238 | 1.3 | 98.36 | 99.993 | |
| 9 | 2,225 | 0.75 | 0 | 99.96 | 100 | .20 GPM $H_2O$ flow |
| 10 | 6,575 | 7.0 | 0 | 99.89 | 100 | |
| 11 | 7,750 | 7.0 | 0 | 99.90 | 100 | |
| 12 | 3,950 | 4.3 | 0 | 99.89 | 100 | |

## 4. A TWO-STAGE WATER/FREON SYSTEM FOR $N_2O_4$ VAPOR SCRUBBING

In order to obtain information of a very preliminary nature, a scrubbing system was set up as shown in Figure 38. The objective was to determine the absorption efficiency of the two-stage water/freon scrubber. The first stage consisted of a tower packed with 1/4 inch Rachig rings over which plain water flowed to remove approximately 90% of the $NO_x$ from the pregnant $N_2O_4$ gas stream. It was decided to use $N_2O_4$ in lieu of NO because of the known previously established information that after scrubbing in $H_2O$ the ratio of NO to $NO_2$ is approximately 10 or 11 to 1. Further, this situation will be more in keeping with the conditions that will prevail on site of vapor removal during the shuttle loading operation. The second stage was simply a two-foot high tower packed to a depth of 18" with 1/2 inch quartz pebbles. The purpose of the pebbles was to provide a longer contact time for the gas bubbles entering the tower.

Gas samples were collected at three points, i.e., the exit lines, both from the $H_2O$ scrubber and from the freon tower, as well as from the inlet gas line. A drying stage was not included.

Three runs were made and the results are shown in table 22.

The efficiencies of both the water and the freon towers are given in columns 5 and 6. The overall efficiencies are given in column 7 for the two-stage system. Column averages are in the bottom line.

The efficiency of the freon tower in Run 1 was only 57.3% on the first pass with fresh freon and drops off very rapidly in the second and third pass through the column as the freon becomes rapidly saturated with $NO_x$ vapors.

In Run 1, (fresh freon in second stage tower) the overall efficiency was 99.4%. In Runs 2 and 3 (used freon) the overall efficiency was reduced to 98.7% and 91.7% indicating a very limited usage with no recirculating capability as was expected. The overall efficiency in Run 1 (99.4%) was high but does not meet the expectations

TABLE 22

SUMMARY OF TWO STAGE, WATER/FREON, RUNS

| Column 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|
| Run # | NOx Inlet Gas ppm | NOx outlet from $H_2O$ Scrubber ppm | NOx outlet from freon tower, ppm | Absorption Efficiency % | Absorption Eff. in 2nd stage, % | Overall System Eff. | Comments |
| 1 | 29,000 | 445 | 190 | 98.4 | 57.3 | 99.4 | Fresh freon in tower 1st pass |
| 2 | 34,000 | 1,030 | 840 | 97.5 | 18.4 | 98.7 | Used freon- 2nd pass |
| 3 | 18,000 | 1,700 | 1,500 | 90.6 | 11.8 | 91.7 | used freon - 3rd pass |
| | Column averages | | | 95.5 | 29.2 | 96.6 | |

Schematic Showing the Two Stage Water/Freon System

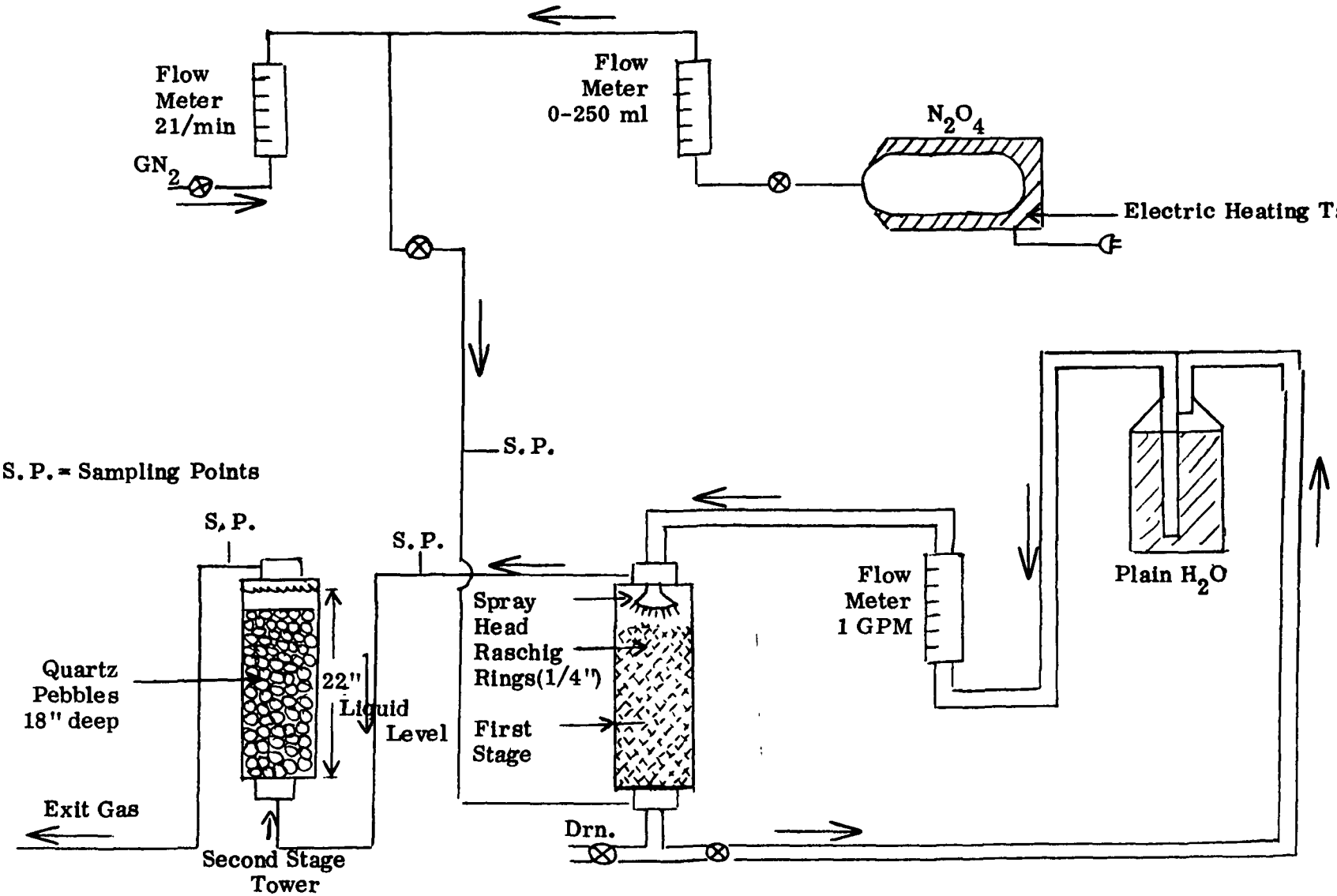



Figure 38

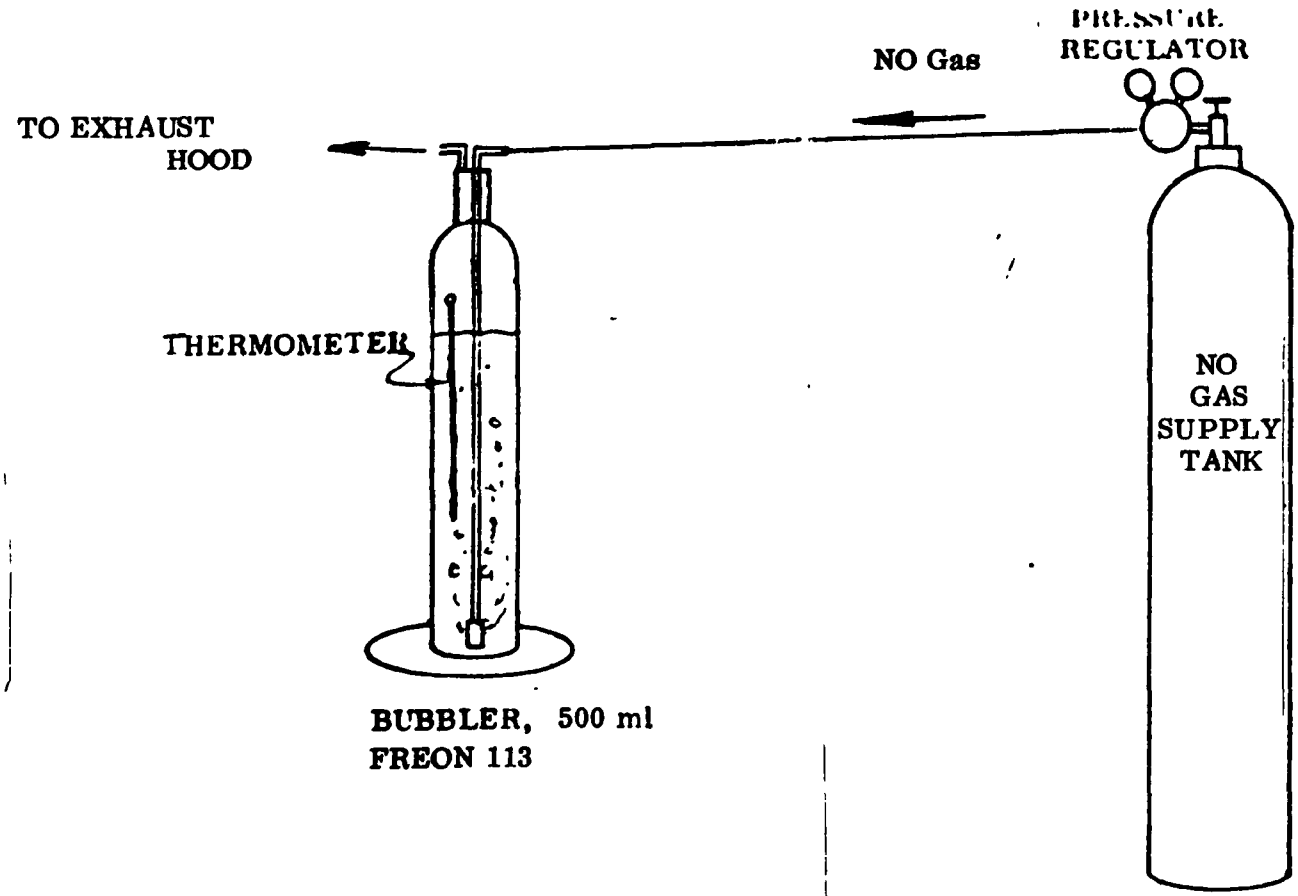
for a two stage system. It is believed that both economically and operationally more satisfactory results are attainable with other methods. For this reason effort was directed to the other methods.

The conclusion reached was: neither the one stage freon system nor the two stage water/freon system, is considered adequate for absorbing the $N_2O_4$ vented vapors to the OSHA 5 ppm limit.

Solubility of NO Gas in Freon

The solubility of NO gas in water is given in the chemical handbooks as 7.34 parts per 100 parts of $H_2O$ at 0°C, or 2.4 parts in hot $H_2O$ or 0 parts at 100°C. This fact accounts largely for the poor absorption efficiency of wet scrubbers for eliminating NO from industrial effluents when plain $H_2O$ is used as scrubber liquor. The solubility of NO was reported to be "good" in freon but no figures were readily available. In order to determine the solubility (approximately) of NO in freon a very simple test was set up. The set up, shown in Figure 39 was to bubble NO at room temperature into freon 113 until saturation (or near saturation) was obtained and analyzing the resulting solution for $NO_x$. The test showed that approximately 5500 ppm NO were held in solution by the freon at 26°C. The conclusion reached was that though the solubility of NO is higher than in $H_2O$, it is still too limited and its use as a scrubber liquor would not be practical. Nevertheless, it was deemed worthwhile to obtain the actual information.

Two runs were made using freon for the scrubber liquor in a single stage system. Also three runs were made in a two-stage system using a water/freon combination. The results appear in the following sections.




Schematic Showing NO - Freon Saturation Apparatus

Figure 39

Use of Freon in a Packed Tower (one stage system)

In Figure 40, is shown schematically the set up for a single stage freon scrubber. The set up is identical to the water scrubber except that the freon 113 was not recirculated through the tower. The freon flowed at the rate of 0.15 gpm over the 27 inch depth of 1/4 inch Raschig rings. The objective was to determine the absorption efficiency of this system.

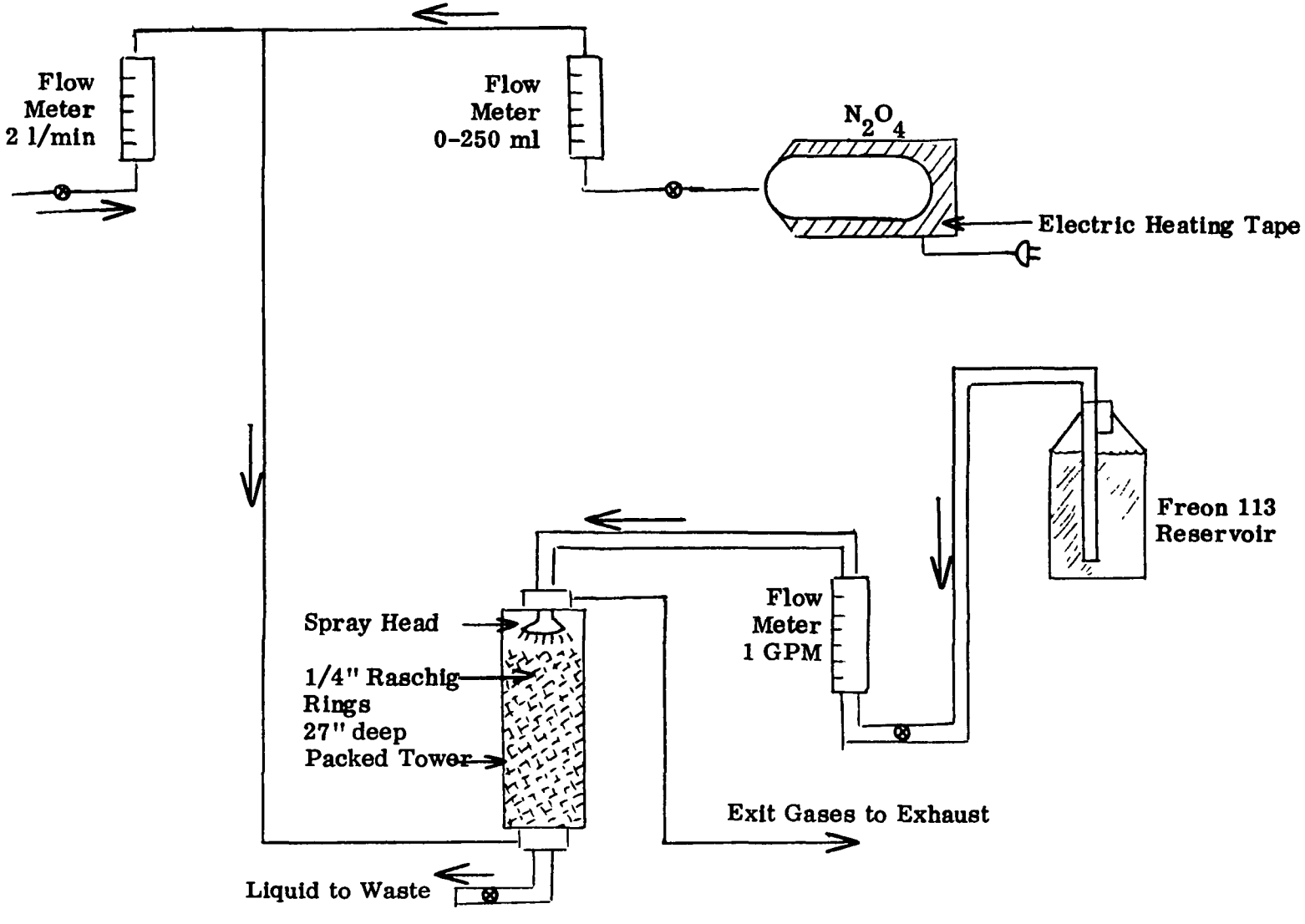
Two runs were made with the results as shown in Table 23.

TABLE 23

| Run # | $NO_x$ inlet Gas, ppm | $NO_x$ outlet Gas, ppm | Absorption Efficiency percent | Comments |
|---|---|---|---|---|
| 1 | 33,000 | 2,420 | 92.7 | Freon not recirculated |
| 2 | 11,500 | 800 | 92.1 | Freon not recirculated |

From Table 23, it is seen that absorption efficiency for a one pass operation just exceeds 92%. This is approximately the same as for plain water runs. However, efficiency may be expected to decrease drastically in a recirculating mode of operation. As the solubility saturation point of $NO_x$ is being approached the efficiency will approach zero percent and will remain at zero thereafter.

The conclusion reached was that no advantage was gained by using freon in lieu of water for scrubbing. Rather, the high cost of freon would be a bid disadvantage for its use, as well as the inherent problem associated with the waste liquid disposal. Further, its high volatility would incur severe losses of the material.




Schematic Showing the Freon Scrubbing System

Figure 40

## 5. AMMONIUM CHLORIDE

Ammonium Chloride was tested in order to avoid the odor problem associated with ammonium hydroxide, but still take advantage of the reactivity of the ammonium ion. The results were very poor, as is seen in Figure 41.

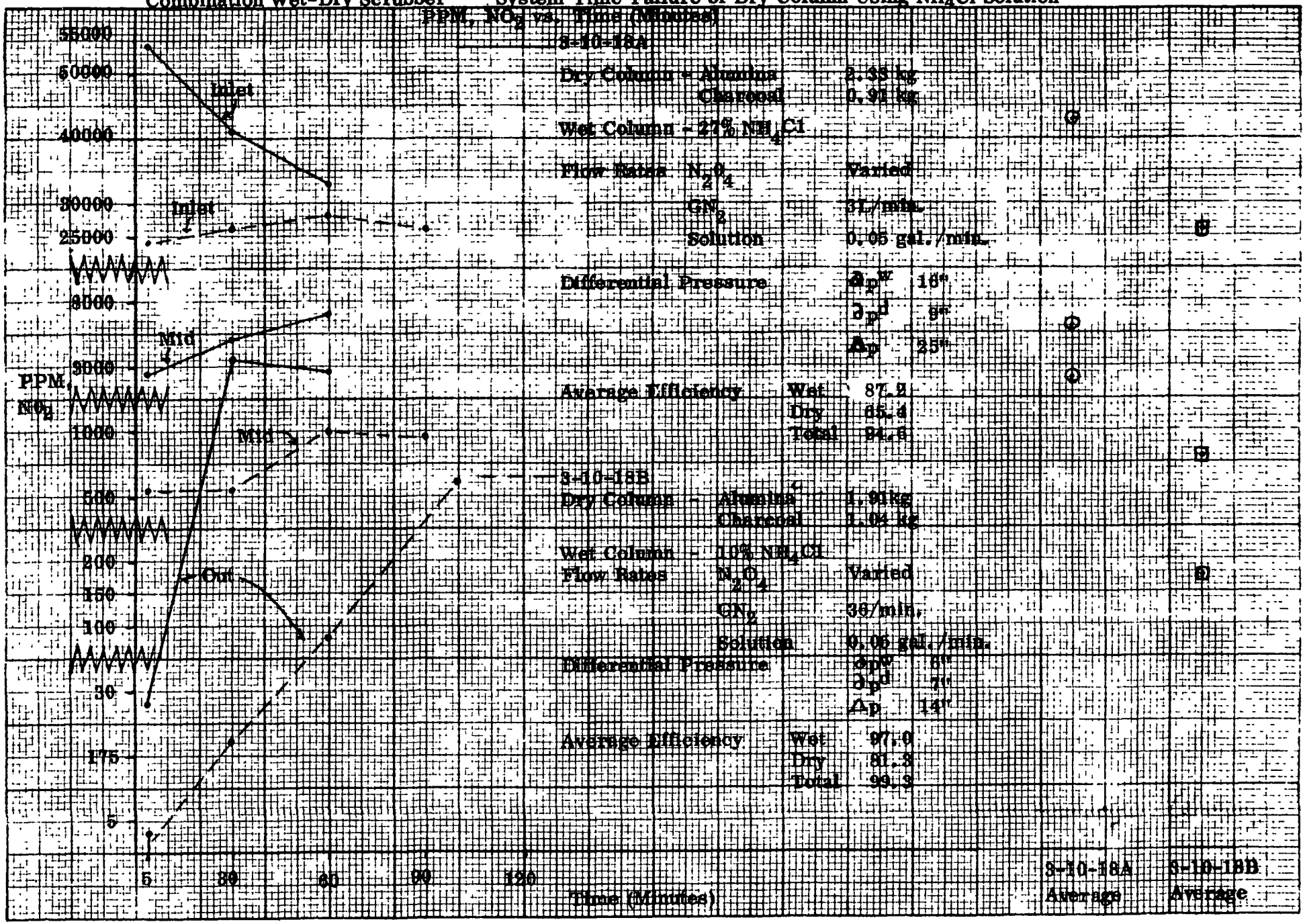

Combination Wet-Dry Scrubber System Time Failure of Dry Column Using $NH_4Cl$ Solution
PPM, $NO_2$ vs. Time (Minutes)
3-10-18A
Dry Column - Alumina 2.33 kg
Charcoal 0.91 kg
Wet Column - 27% $NH_4Cl$
Flow Rates $N_2O_4$ Varied
$GN_2$ 3L/min.
Solution 0.05 gal./min.
Differential Pressure $\partial p^w$ 16"
$\partial p^d$ 9"
$\Delta p$ 25"
Average Efficiency Wet 87.2
Dry 65.4
Total 94.6
3-10-18B
Dry Column - Alumina 1.91kg
Charcoal 1.04 kg
Wet Column - 10% $NH_4Cl$
Flow Rates $N_2O_4$ Varied
$GN_2$ 3L/min.
Solution 0.05 gal./min.
Differential Pressure $\partial p^w$ 6"
$\partial p^d$ 7"
$\Delta p$ 14"
Average Efficiency Wet 97.0
Dry 81.3
Total 99.3
Inlet
Mid
Out
PPM, $NO_2$
Time (Minutes)
3-10-18A Average
3-10-18B Average

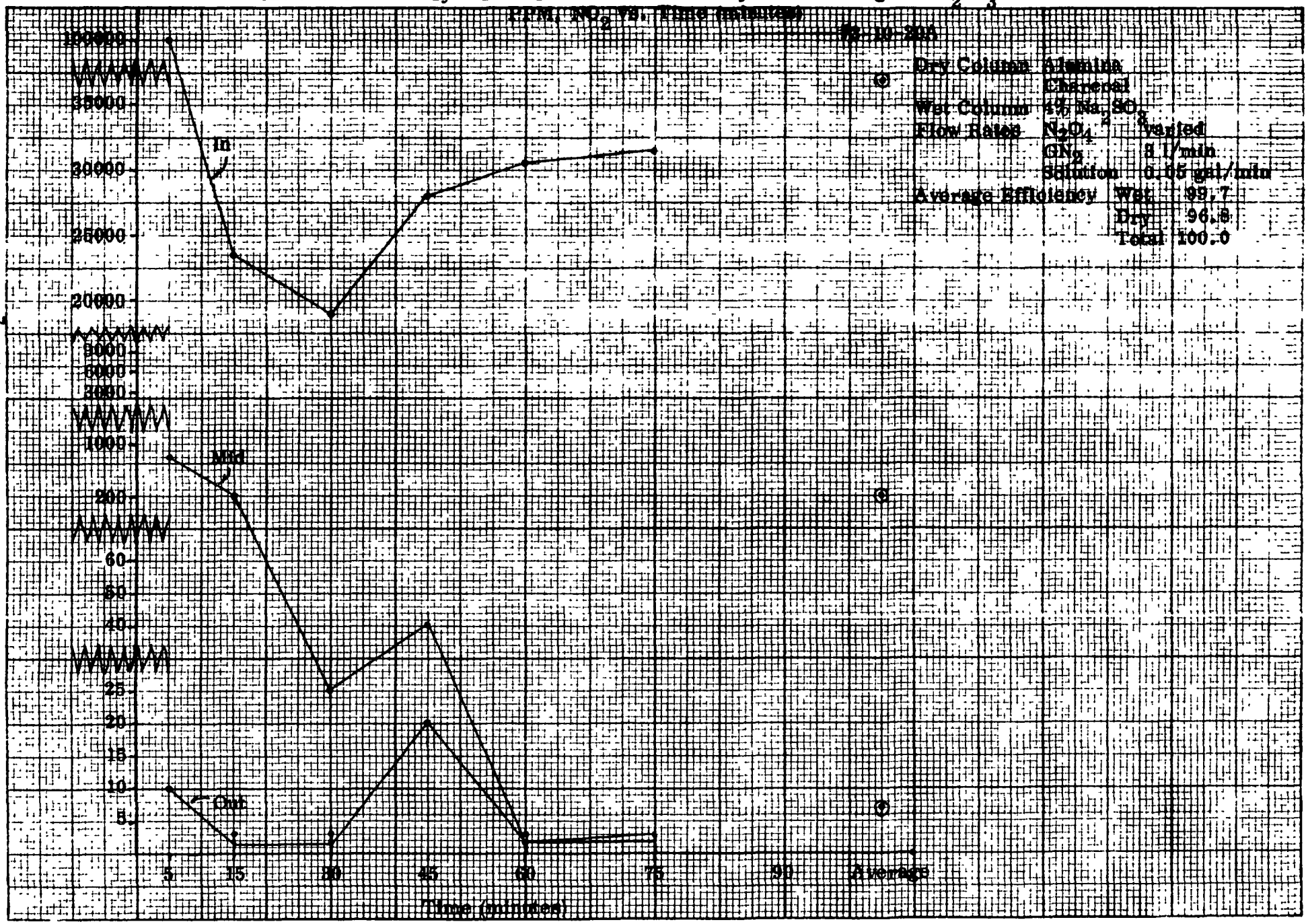
FIGURE 41

## 6. SODIUM SULFITE

Sodium sulfite, as noted in the INTRODUCTION, was reported to be an effective agent for scrubbing $NO_2$. Thus, experiments as delineated in Figures 42 and 43 were conducted. As is seen the results were very impressive - particularly so when a dry scrubber is used in the second stage.

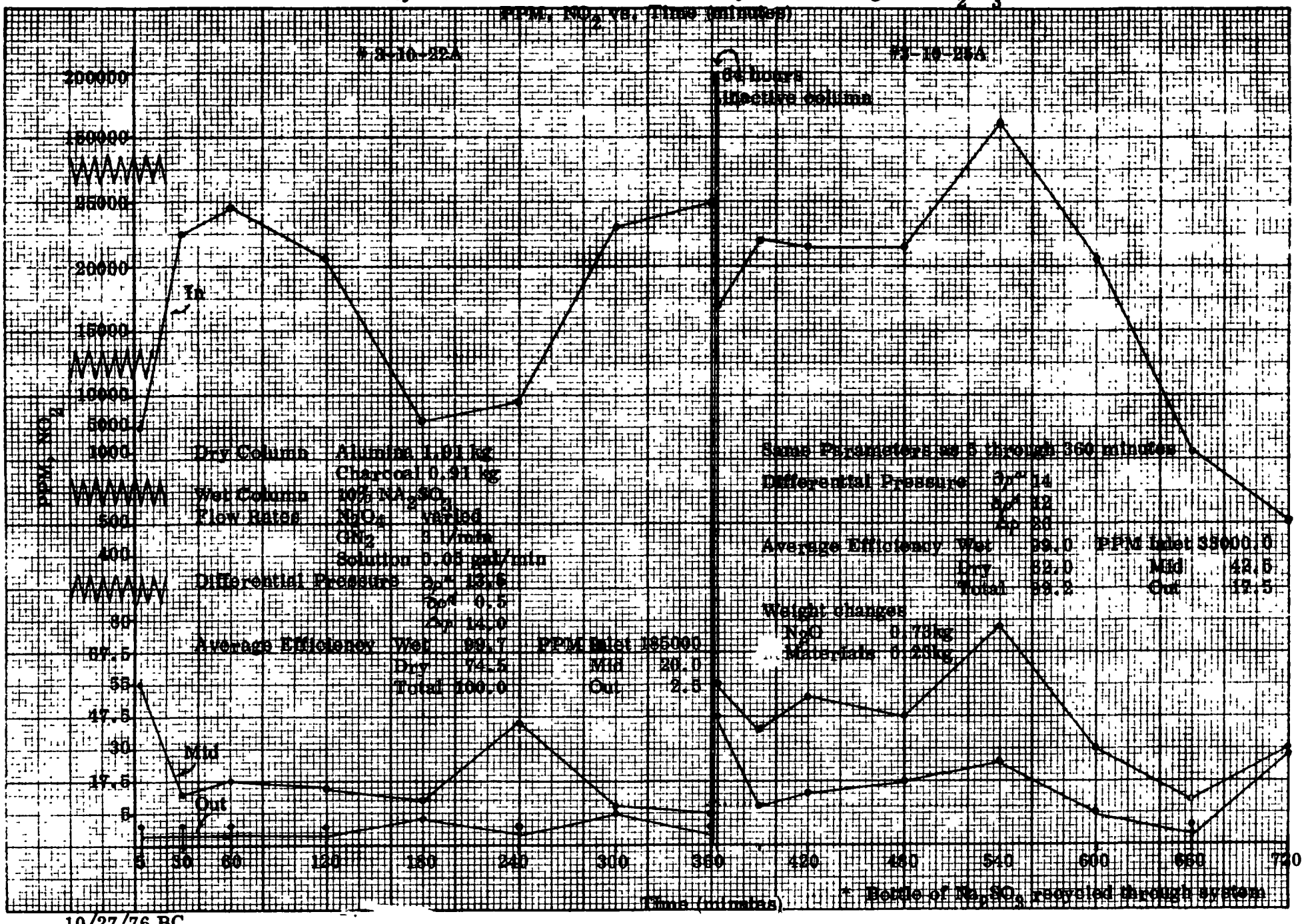
PROGRESS 20 X 20 TO THE INCH Z-2282
7 X 10 INCHES

## Combination Wet-Dry Scrubber Time Failure of Dry Column using 4% $Na_2SO_3$ Solution




10/22/76 BC

FIGURE 42



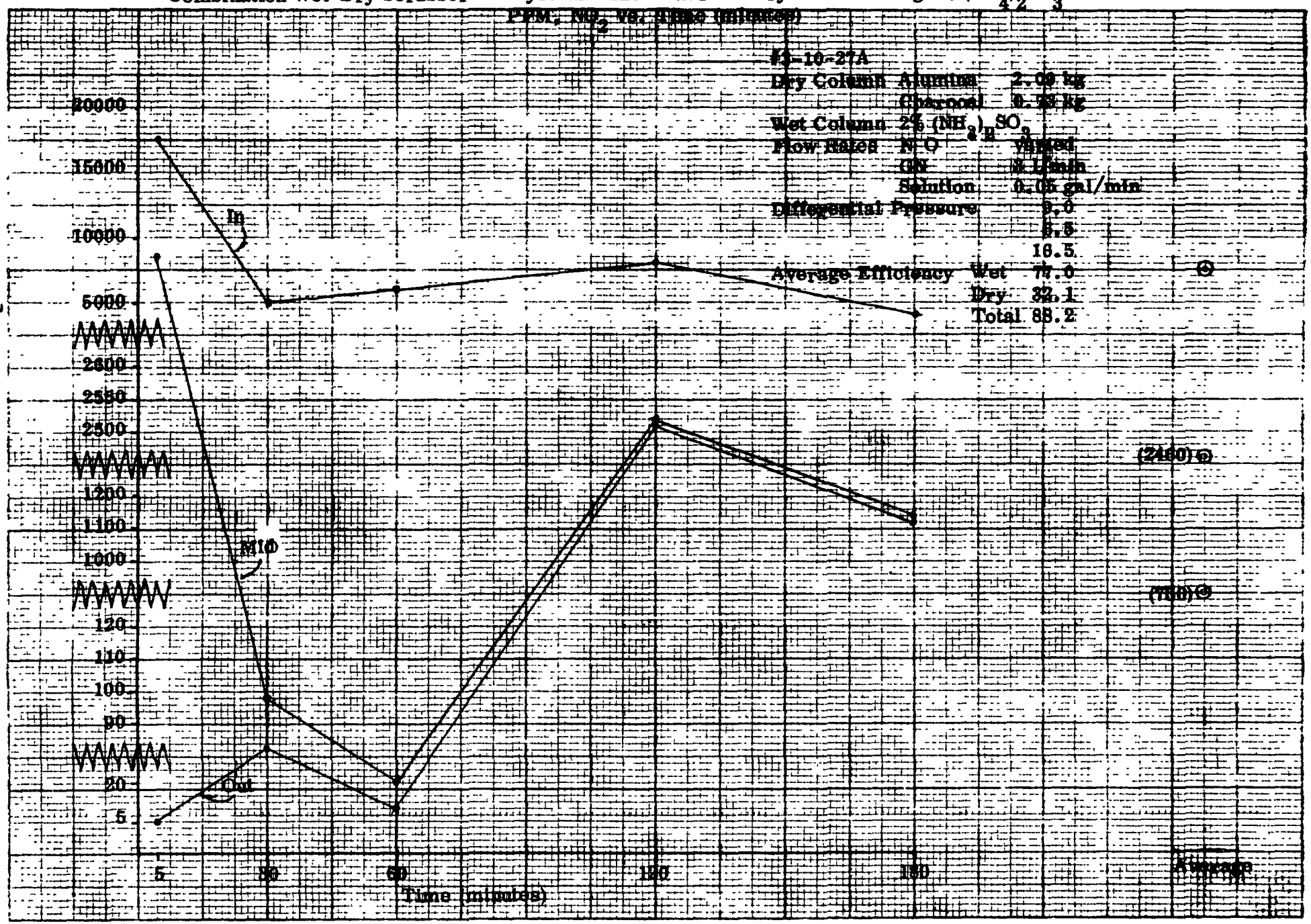

10/27/76 BC

FIGURE 43

## 7. AMMONIUM SULFITE

As is seen in Figure 44, ammonium sulfite seems to be very ineffective. However, the concentration of the reagent was very low and this experiment should be repeated.

PROGRESS 20 X 20 TO THE INCH Z-2282




11/1/76 BC

FIGURE 44

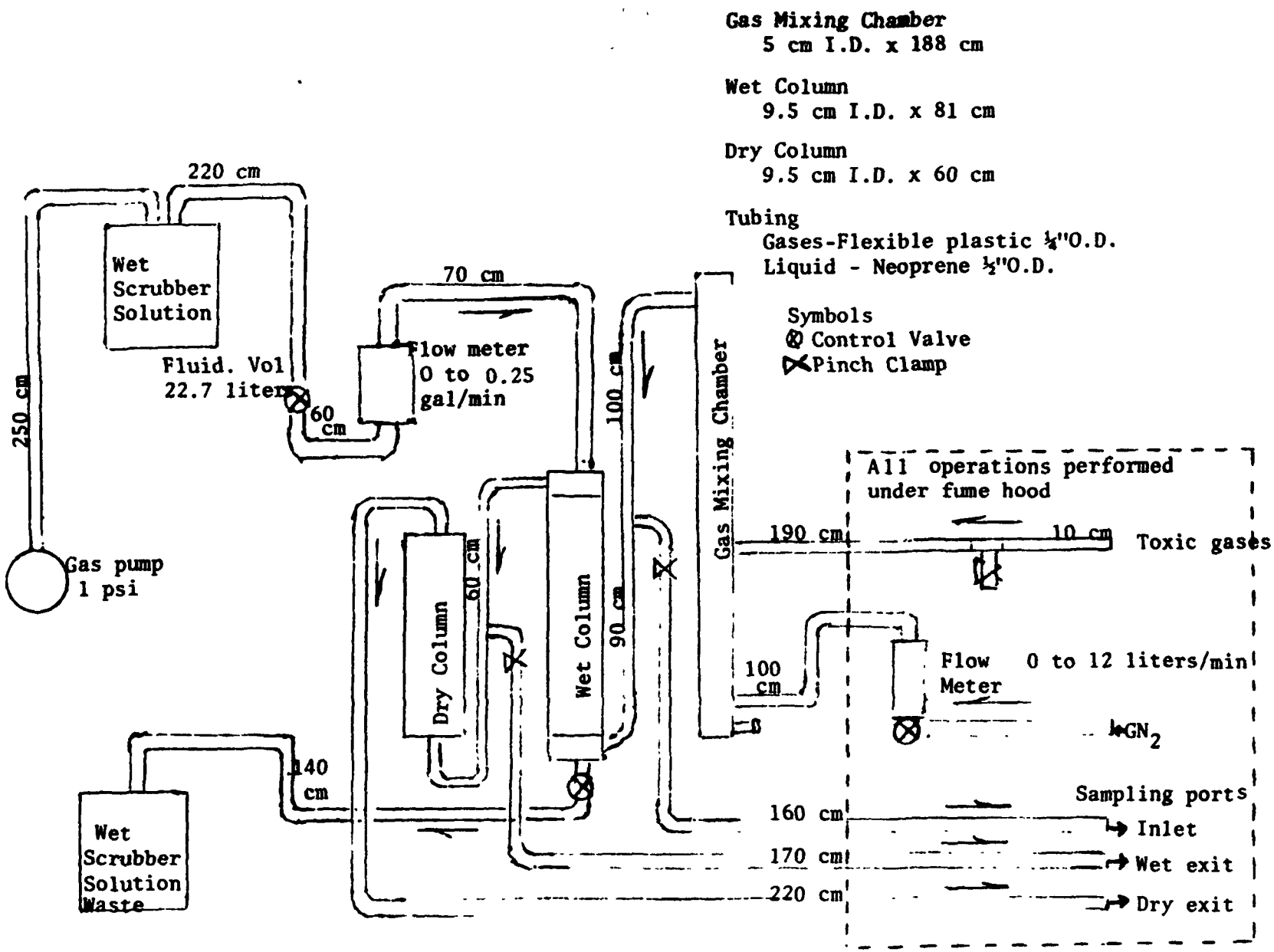

Gas Mixing Chamber
5 cm I.D. x 188 cm
Wet Column
9.5 cm I.D. x 81 cm
Dry Column
9.5 cm I.D. x 60 cm
Tubing
Gases-Flexible plastic ¼"O.D.
Liquid - Neoprene ½"O.D.
Symbols
Control Valve
Pinch Clamp
220 cm
Wet Scrubber Solution
Fluid. Vol 22.7 liters
250 cm
60 cm
70 cm
Flow meter 0 to 0.25 gal/min
100 cm
Gas Mixing Chamber
All operations performed under fume hood
190 cm
10 cm
Toxic gases
Gas pump 1 psi
Dry Column
60 cm
Wet Column
90 cm
100 cm
Flow Meter
0 to 12 liters/min
GN2
140 cm
Wet Scrubber Solution Waste
Sampling ports
160 cm
Inlet
170 cm
Wet exit
220 cm
Dry exit

Figure 44

# CHAPTER 5

# SUMMARY AND CONCLUSIONS

1. Wet scrubbers have far greater capacity for $NO_2$ and MMH absorption than dry scrubbers.

2. The scrubbing liquors for $N_2O_4$ are ranked in descending order as to overall practicality and efficiency for shuttle operations.

    1. Sodium sulfite in water
    2. Triethanolamine in water
    3. Ammonium hydroxide in water
    4. Sodium hydroxide in water
    5. Water
    6. Oxygen in water and caustic
    7. Ozone in water and caustic
    8. Hydrogen peroxide in water and caustic
    9. Sodium hypochlorite in water

3. Second Stage dry scrubbers work effectively in conjunction with sodium sulfite and ammonium hydroxide wet scrubbing liquors.

4. Triethanolamine is the best scrubbing liquor for $N_2O_4$. However, N-nitroso-diethanolamine, a potent carcinogen, almost certainly forms as a non-volatile reaction product. Thus very careful handling of the spent liquors is required.

# APPENDIX

MARTIN MARIETTA CORPORATION

Denver Division

ENGINEERING PROPULSION LABORATORY

# TEST REPORT

TEST NUMBER H40679

CONTRACT FIT P.O. 127676 and 128140

# DEVELOPMENT TESTS OF MMH AND $N_2O_4$ WET SCRUBBERS

September 1976

PREPARED BY:

T. D. Reisert 9-15-76

T. D. Reisert, Lead Test Engineer
Engineering Propulsion Laboratory

PREPARED FOR:

Florida Institute of Technology

Melbourne, Florida

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FIGURE 2 Wet Scrubber Schematic ..... A-28

FIGURE 3 Off Gas Sampling Set-up ..... A-29

## 1.0 INTRODUCTION

A two part test program to evaluate wet scrubber systems for Monomethylhydrazine (MMH) vapors and Nitrogen Tetroxide ($N_2O_4$) vapors has been completed at the Martin Marietta Engineering Propulsion Laboratory in Denver, Colorado. Testing was conducted in August 1976 under the direction of the Florida Institute of Technology (FIT). For both propellants, vapors were mixed with a controlled nitrogen gas flow and flowed from the lower part of the scrubber through the bed material and the scrubber liquor and out the top of the scrubber. The scrubber liquor was sprayed onto the top of the packing bed and drained off the bottom. Analysis of input gases and exit gases to the scrubber were made principally using wet chemical techniques provided by FIT. Occasional checks of the data were made using Drager tubes and an Olfactron toxic gas detector. For all tests, the scrubber liquor flow rate was approximately 10.4 gallons per minute. For MMH tests, input concentrations varied from 45 ppm to 10,000 ppm for nitrogen gas flow rates of 20 to 10 to 200 scfm. Packing bed heights of four-feet and seven-feet were used in the scrubber.

## 2.0 TEST SET-UP AND EQUIPMENT LIST

The test set up used for these tests is shown in the photograph of Figure 1, and the schematic of Figure 2. The scrubber was 24 inches in diameter and 11 feet high. It was made from an existing stainless steel flanged cylindrical section available at the Engineering Propulsion Laboratory (EPL). The packing material in the bed of the scrubber consisted of 0.75 inch commercially available ceramic saddles suspended above the bottom of the scrubber column on a coarse screen. Packing bed heights of four-feet and seven-feet were used during these tests. Scrubber liquor was mixed and stored in an external tank and distributed uniformly on the top of the ceramic saddles in the scrubber bed. The scrubber liquor then drained back into the storage tank for recirculation. A demister consisting of a coarse screen was installed in the entrance to the vent pipe of the scrubber to minimize escape of corrosive liquid droplets from the scrubber vent.

Input MMH and $N_2O_4$ vapor to the scrubber were vapor to the scrubber were vaporized in a container located in a hot water bath and in the heated inlet lines to the scrubber. Input vapors were blended with ambient temperature nitrogen gas at selected flow rates prior to inlet gas sampling.

Input gas samples for the wet chemistry analysis were taken with a syringe inserted in the input gas flow just outside the scrubber wall. Output gas samples were taken with a syringe inserted in vent pipe upstream of the gas exit.

Drager tube measurements were made by inserting the tubes in the sampling ports used for obtaining the wet chemistry samples.

Olfactron meter measurements of the output gas during $N_2O_4$ tests were made through a tube extending into the center of flow of the vent gas.

## 2.1 Test Equipment List

| | |
|---|---|
| Recirculating Pump | Chempump seal-less pump |
| | Model GA-1 1/2K 7511-ls |
| | 230/460 volt 3 phase 3450 RPM |
| | 7.7/3.8 amps 2.5 KW full load rating |
| | Manufactured by Crane Chempump Division, Warrington, PA 18970 |
| Teledyne Toxkc Vapor Detector | - Olfactron Model 6110 |
| Flow Nozzles | 0.112 inch calibrated |
| | 0.353 inch calibrated |
| Scrubber Bed Material | 0.75 inch ceramic saddles, commercial grade |

## 3.0 TEST DESCRIPTION FOR MMH

Ten MMH test runs were made with the wet scrubber. Four runs were made with a scrubber bed height of four feet and six runs were made with a scrubber bed height of seven feet. The strength of the scrubber liquor during these tests varied from .71 percent available chlorine to 5.09 percent and was always changing during test operation. Preliminary tests of the scrubber bed with water indicated that the differential pressure across the scrubber was small (less than 1 inch of water) and the decision was made by the FIT representative to increase the scrubber liquor flow to the maximum obtainable with the existing equipment (approximately 20.4 gpm) for all test runs. Test operating data and results obtained for the MMH runs were presented in Table I.

### 3.1 Test Run #1

The initial test run was made with a nitrogen gas flow rate of 20 scfm and inlet gas concentrations that varied from 280 ppm to 650 ppm of MMH. Wet chemistry analysis of the scrubber outlet gas indicated MMH concentrations of 2.9 to 7.5 ppm or absorption efficiencies of 98.57 to 99.35 percent.

### 3.2 Test Run #2

For this test run, the nitrogen gas flow rate was increased to 100 scfm and operated for approximately two hours at inlet concentrations of 340 ppm to 650 ppm of MMH. Wet chemistry analysis of the scrubber outlet gas indicated MMH concentrations of 1.2 to 1.7 ppm. Analysis of outlet gas by Drager tubes taken at the same time indicated similar concentrations. Based on these results, absorption efficiencies varied from 99.62 to 99.79 percent.

### 3.3 Test Run #3

Nitrogen gas flow rate was increased for this run to 200 scfm. Inlet gas concentrations over approximately one hour were measured to be from 120 ppm to

410 ppm of MMH. Outlet gas concentrations were measured by both wet chemistry and Drager tubes to be 2.0 to 2.4 ppm of MMH. Absorption efficiencies were calculated to vary from 98.17 to 99.41 percent for these conditions.

### 3.4 Test Run #4

For the final run of the day with a four-foot scrubber bed height, the nitrogen gas flow rate was reduced to 20 scfm and the MMH concentration of the inlet gas was measured to be 380 ppm. Analysis of the outlet gas by the wet chemistry technique indicated 2.4 ppm of MMH and the Drager tube indicated 2.0 ppm. These results indicate an absorption efficiency of 99.37 percent. Analysis of the scrubber liquor at this time indicated that it was percent and should be replaced according to direction from the FIT representative.

### 3.5 Test Run #5

Prior to making this run, the scrubber bed of saddles was increased from four feet to seven feet in height by removing the top flange of the scrubber and pouring in the additional ceramic saddles. The hypochlorite solution used for previous test runs was drained from the storage tank and replaced with 200 gallons of fresh solution with a strength of 5.09 percent available chlorine. The nitrogen gas flow rate was set at 430 scfm. It was noted that at this flow rate some moisture was getting through the demister and the vent system for the scrubber was saturated with chlorine. This made it difficult to obtain a true sample of the outlet gas and could be the reason why the Drager tubes indicated no MMH in the outlet gas while the wet chemistry analysis indicated 8.6 to 25 ppm. The wet chemistry analysis can be affected by the presence of chlorine. Even with these complicating interactions the absorption efficiency was calculated to vary from 87.5 to 97.86 percent.

### 3.6 Test Run #6

Nitrogen gas flow rate was reduced to 20 scfm to obtain data from the seven

foot scrubber bed that can be compared with data from the previous tests of the four foot scrubber bed. One sample each of the inlet and outlet gases were taken for wet chemistry analysis and a Drager tube measurement of outlet gas was made. There was some question as to the validity of the inlet sample taken and a decision was made to purge the system with nitrogen gas for at least 30 minutes at 100 scfm flow rate to cleanup the inlet.

### 3.7 Test Run #7

Prior to starting this test run, 80 gallons of water was added to the scrubber liquor to reduce the strength to 3 percent available chlorine. The initial inlet gas sample indicated 10,000 ppm of MMH and the corresponding outlet gas sample indicated 4.5 ppm of an absorption efficiency of 99.96 percent. Prior to taking a second sample, the MMH metering valve was partially closed which gave 950 ppm at the inlet and 2.5 ppm at the scrubber outlet. Drager tube analysis of outlet gas for both samples indicated no MMH present. After the second gas sample was taken, the MMH input valve was closed completely and the nitrogen gas purge continued for several hours to clean up the system.

### 3.8 Test Run #8

During this test run, additional data were obtained at a nitrogen gas flow rate of 20 scfm. The results of three sets of gas samples taken over a period of one hour indicated absorption efficiencies of 99.49 to 99.93 percent. Again Drager tube analysis of the output gas indicated no MMH present.

### 3.9 Test Run #9

For this run, nitrogen gas flow rate was increased to 100 scfm and three sets of gas samples were obtained over a one hour period. Results of wet chemistry analysis indicated input gas concentrations from 315 to 1380 ppm of MMH and output gas concentration from 3.4 to 7.5 ppm which resulted in absorption efficiencies of 98.92 to 99.46 percent. Drager tube analysis of the output gas indicated no MMH present.

### 3.10 Test Run #10

This run was similar to previous runs except $GN_2$ flow was increased to 200 scfm. Test results indicated absorption efficiencies of 97.78 percent for an input concentration of 45 ppm to 98.99 percent for an input concentration of 940 ppm. Drager tube analysis of samples taken at corresponding times indicated from 0 to .25 ppm of MMH which was considerably less than the concentrations indicated by wet chemistry analysis. A sample of the scrubber liquor taken during this final run was analyzed and the concentrations of available chlorine at this time was established at .71 percent. After this run was completed, the scrubber liquor was drained from the storage tank and the entire scrubber system flushed with water.

## 4.0 TEST DESCRIPTION FOR NITROGEN TETROXIDE

Fifteen $N_2O_4$ test runs were made with the wet scrubber. Two runs were made with a scrubber bed height of four feet and thirteen were made with a bed height of seven feet. For these runs, dry sodium hydroxide pellets were mixed with water to obtain an initial liquor strength of 7.52 percent. This strength gradually decreased to .48 percent during run 13. Prior to run 14, additional dry sodium hydroxide and water were added to the scrubber liquor to increase the strength to 1.4 percent. As in the MMH test runs, scrubber liquor flow was maintained at approximately 20.5 gallons per minute for all runs. Test operating data and results obtained for the $N_2O_4$ runs are presented in Table II.

### 4.1 Test Run #1

The initial run was made with a nitrogen gas flow of 100 scfm with the scrubber bed height of four feet. Input gas analysis by the wet chemistry technique indicated 637 ppm of $N_2O_4$. Output gas analysis by the same technique indicated 232 ppm of $NO_x$ which resulted in an absorption efficiency of only 63.57 percent.

### 4.2 Test Run #2

Nitrogen gas flow rate was reduced to 20 scfm and input gas concentrations of $N_2O_4$ were varied from 862 to 5000 ppm. Output gas analysis by the wet chemistry technique indicated that gas samples taken at the same time as the input gas samples varied from 200 to 253 ppm of $NO_x$ which resulted in absorption efficiencies from 76.56 to 94.9 percent. The higher the input concentration, the higher the efficiency obtained. Two Drager tube measurements of the output gas were in agreement with wet chemistry results.

### 4.3 Test Run #3

Prior to starting this run the scrubber bed height was increased from four feet to seven feet. The nitrogen gas flow rate was continued at 20 scfm and two

sets of gas samples were taken 20 minutes apart. The measured input concentrations were 4990 and 4890 ppm and the output concentrations 152 and 155 ppm of $NO_x$. These data resulted in absorption efficiencies of 96.93 and 96.83 percent which compare with 94.9 percent for the four foot scrubber bed.

4.4 Test Run #4

This was the last run of the day. Nitrogen gas flow rate was increased to 50 scfm and one set of gas samples was taken. For an input gas concentration of 3600 ppm of $N_2O_4$ an outlet gas concentration of 166 ppm was obtained which resulted in an absorption efficiency of 95.39 percent.

4.5 Test Run #5

The purpose of this test run was to determine the effect of adding oxygen to the inlet gas flow. Prior to conducting this test run, the $N_2O_4$ container was refilled. Nitrogen gas flow rate was established at 50 scfm. Two sets of gas samples were taken at input concentrations of 1250 and 3625 ppm with no oxygen added. Outlet gas sample analysis indicated 150-167 ppm of $NO_x$ or 88 and 95.39 percent absorption efficiency. Oxygen was then added to the input flow at 5 scfm and 3 sets of gas samples taken of inlet and outlet gas. These samples indicated absorption efficiencies of 94.01, 95.12 and 97.56 percent for input gas concentrations of 3125, 3950, and 4180 ppm of $N_2O_4$

4.6 Test Run #6

This test run was made to determine the absorption efficiencies of the scrubber for 100 scfm nitrogen gas flow for several input concentrations. Six sets of gas samples were taken with resulting efficiencies of 75 to 96.08 percent. During this run the Olfactron toxic vapor detector was used to monitor the output gas at the same time wet chemistry gas samples were taken. The readings obtained were generally higher than those obtained by the wet chemistry analysis.

## 4.7 Test Run #7

This test run is a continuation of test run 6, after the test was shut down to replenish the supply of $N_2O_4$ in the gas input system. Eight sets of gas samples were taken over a two hour time period with resulting absorption efficiencies of 83.7 to 92.53 percent. Results of output gas concentrations from the Olfactron vapor detector were in better agreement with the results of the wet chemistry analysis than on test run 6.

## 4.8 Test Run #8

This test run was made to determine the absorption efficiencies for 200 scfm nitrogen gas flow for a range of $N_2O_4$ input concentrations. Twelve sets of gas flow for a range of taken over a three hour time period. The first ten sets indicated absorption efficiencies from 72.85 to 88.16 percent. The last two samples indicated much lower values which can probably be attributed to not taking a valid gas sample. An attempt was made during this run to use the Olfactron vapor detector to measure $NO_x$ concentration as on the previous run. In all sampling attempts, the magnitude exceeded 500 ppm which was the maximum that could be registered on the instrument. Possible saturation of the sampling tube with scrubber liquor "blow-by" of the demister may be the cause of the unexpected high readings.

## 4.9 Test Run #9

This test run was the first in a series of attempts to obtain high input concentrations of $N_2O_4$ for low nitrogen gas flow rates. The nitrogen gas flow rate was reduced to 50 scfm without changing the control values of the $N_2O_4$ supply. A set of gas samples was taken which indicated an input of 2530 ppm and an absorption efficiency of 89.09 percent.

4.10 Test Run #10

Nitrogen gas flow rate was reduced to 20 scfm again without changing the values of the $N_2O_4$ supply. One set of gas samples was taken which indicated an input of 5800 ppm and an absorption efficiency of 94.56 percent. The $N_2O_4$ supply container was exhausted after taking the set of samples and the test interrupted.

4.11 Test Run #11

When the supply container was refilled with $N_2O_4$, the nitrogen gas flow was reestablished at 20 scfm and $N_2O_4$ input adjusted for a large concentration. After each set of samples was taken the $N_2O_4$ input was increased. For this run, input concentrations were measured to vary from 13,800 ppm to 18,000 ppm and absorption efficiencies were calculated to be 98.77 and 99.22 percent.

4.12 Test Run #12

Nitrogen gas flow was reduced to 10 scfm which was the minimum flow operating condition that could be obtained with the existing test setup. Three sets of gas samples indicated input concentrations from 9250 to 14,650 ppm of $N_2O_4$ and absorption efficiencies of 98.83 to 99.51 percent.

4.13 Test # 13

This run was made to determine the absorption efficiencies of the scrubber for a high gas flow rate and a very low input of $N_2O_4$ vapor. Nitrogen gas flow rate was established at 200 scfm and $N_2O_4$ in the inlet gas was measured to be 300 ppm. The output gas was analyzed and found to have 88.5 ppm of $NO_x$ or 70.5 percent absorption efficiency.

4.14 Test Run #14

This run was similar to run 13 escept the input concentration was reduced to 52.5 ppm. The output concentration was measured to be 32 ppm or an absorption efficiency of 39 percent.

4.15 Test Run #15

The highest concentration of $N_2O_4$ in the input gas obtained prior to this test run was 18,000 ppm. In order to increase this magnitude to greater than 100,000 ppm, the discharge line from the $N_2O_4$ container was attached to the bottom or liquid side and depended on the heated inlet line for vaporization. The temperature of the water bottle around the $N_2O_4$ container was increased above 120°F and the pressure in the container was allowed to increase to approximately 25 psig. When this run was started, the $N_2O_4$ was injected in a nitrogen gas flow of greater than 100 scfm and then the flow rate was reduced to 200 scfm which was the minimum flow rate attainable without scrubber liquor backing up in the inlet line. An inlet gas sample taken approximately four minutes after the start indicated an input concentration of 410,000 ppm. An outlet gas sample taken at the same time indicated 900 ppm of $NO_x$ or an absorption efficiency of 99.78 percent. Two other sets of samples were taken before the $N_2O_4$ supply was exhausted. Absorption efficiencies for the final two samples indicated 99.6 and 99.69 percent.

## 5.0 TRACE COMPONENT ANALYSIS

### 5.1 General

The off gas from the scrubber during MMH runs was trapped at liquid nitrogen temperatures. The trapped material was subjected to gas chromatograph analysis utilizing column and conditions developed for analysis of the chemical side products produced during the synthesis of MMH. The reactant chemicals involved in the synthesis of hydrazine are identical to those which would be involved in the water-hypochlorite oxidation utilized in the wet scrubber to remove the monomethyl hydrazine. These reactive chemicals are:

| | |
|---|---|
| Chloramine | $NH_2Cl$ |
| Hypochlorite Ion | $ClO^-$ |
| Monomethyl Hadrazine | $CH_3\text{-}NH\text{-}NH_2$ |
| Hydroxide Ion | $OH^-$ |
| Water | $H_2O$ |
| Monomethylamine | $CH_3NH_2$ |

The differences between the scrubbing reaction and the synthesis reaction are in the concentration of the various reactants. The same types of low level products should exist in both reactions and only the concentration balance between the products should be different.

### 5.2 Off Gas Sampling

A sampling apparatus was setup as shown schematically in Figure 3. A slight vacuum was drawn on the system to induce flow of gas from the scrubber through the sampling system. The flow was adjusted to approximately one liter per minute by adjusting the source vacuum level. The incoming gas was first drawn through a bed of pyrex glass wool to remove entrained liquid droplets. The temperature was monitored at this point to detect any large deviations. The gas then passed through the cold trap where most of the water and organic contamin-

ants were condensed from the gas phase. Table III shows the flows and temperatures during off gas sampling.

After completion of the gas sampling, the sampling assembly was transferred in the cold condition to the chemistry laboratory. The cryogenic trap was allowed to warm to ambient temperature and the trapped material, now liquid were obtained. The liquid was transferred to a glass stoppered flask for retention and analysis. The cryogenic trap assembly was washed with several portions of distilled water and dried with a nitrogen gas purge to ready it for the next test.

5.3 Gas Chromatograph Analysis of Off Gas

Samples of MMH scrubber off gas products obtained by cryogenic trappings were analyzed with a standard gas chromotograph system employing a flame ionization detector and an all glass inlet and column. The samples were diluted with distilled water to a known volume and 0.5 ml portions were then injected into a six foot glass column containing 80 to 100 mesh Carbopack B coated with 0.8 percent KOH and 4 percent Carbowax 20M. The inlet was held at 150°C and the column oven was programmed from 75° to 150°C at 8° per minute. Three samples from scrubber runs conducted on 8-17-76, 8-18-76, and 8-19-76 were analyzed along with a standard background solution made from fresh NaOCl solution.

The three samples appeared quite similar by gas chromatograph analysis with the sample taken on 8-19-76 being somewhat lower in total products by approximately a factor of two. All samples gave chromatograms of 10 to 15 peaks in approximately the 10 to 100 ppm range in solution (approximately 1 to 10 ppm in the gas coming off the scrubber). The more significant peaks in order of decreasing concentration had approximate retention times (R.T.) of 0.7, 3.0, 1.7, 4.0, 1.4, 5.1, 0.4, 3.5, 6.2, and 7.3. Standards of compounds possibly formed in the scrubber area were analyzed by the gas chromatograph under

identical conditions.

These were:

MMA - R.T. 0.67, $CH_2Cl_2$ - R.T. 2.9, $CHCl_3$ - R.T. 5.9, $CH_3OH$ - R.T. 1.5, MMH - R.T. 4.0, and $CCl_4$ - R.T. 6.3. Although these compounds in some cases compare quite well with retention times of some sample peaks, this in itself is not proof of identification.

## 6.0 CONCLUDING REMARKS

The results of the test runs made with the wet scrubber, indicate that

1. The higher the concentration of the input gas, the higher the absorption efficiency obtained.
2. The lower the gas flow, the higher the absorption efficiency obtained.
3. Increasing bed height increases efficiency.
4. MMH runs using sodium hypochlorite achieved higher absorption efficiencies than $N_2O_4$ runs using sodium hydroxide.
5. Addition of oxygen to the inlet gas for the conditions tested had little or no effect on the absorption efficiency obtained.

## TABLE I

## MMH WET SCRUBBER TEST DATA

Scrubber Bed Height - 4 ft.

Scrubber Liquor - Sodium Hypochlorite Solution

| Run No. | Date 1976 | Time | Scrubber Bed | | Liquor Flow Rate gpm | Liquor Strength % Avail. Chlorine | Storage Tank Temp. °F | $GN_2$ Flow Rate scfm | Temp of MMH Vaporizes °F | Wet Chemistry Analysis | | | Drager Tube Analysis of Outlet Gas, ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | ΔP, in. of water | Temp. °F | | | | | | Inlet Gas ppm | Outlet Gas ppm | Absorb. Effec., Percent | |
| 1. | 8-17 | 0940 | 0 | | 20.4 | 3.0 | | 20 | 190 | 540 | --- | --- | --- |
| | | 0955 | 0 | | 20.4 | | | 20 | 190 | 650 | 4.5 | 99.31 | 0 |
| | | 1017 | 0 | | 20.4 | | | 20 | 190 | 620 | 4.0 | 99.35 | 0 |
| | | 1040 | 0 | | 20.4 | | | 20 | 185 | 280 | 4.0 | 98.57 | --- |
| | | 1100 | 0 | | 20.4 | | | 20 | 180 | 590 | 7.5 | 98.73 | --- |
| | | 1115 | 0 | | 20.4 | | | 20 | 180 | 290 | 2.9 | 99.0 | --- |
| 2. | 8-17 | 1143 | 0 | | 20.4 | | | 100 | 180 | 460 | 1.3 | 99.72 | 1.3 |
| | | 1218 | 0 | | 20.4 | | | 100 | 180 | 340 | 1.3 | 99.62 | 1.0 |
| | | 1245 | 0 | | 20.4 | | | 100 | 181 | 650 | 1.7 | 99.74 | 1.75 |
| | 1315 | 1315 | 0 | | 20.4 | | | 100 | 181 | 560 | 1.2 | 99.79 | 1.7 |
| 3. | 8-17 | 1335 | .2 | | 20.4 | | | 200 | 184 | 120 | 2.2 | 98.17 | 2.2 |
| | | 1403 | .2 | | 20.3 | | | 200 | 186 | 360 | 2.2 | 99.39 | 2.0 |
| | | 1425 | .2 | | 20.3 | | | 200 | 186 | 410 | 2.4 | 99.41 | 2.2 |
| 4. | 8-17 | 1442 | 0 | | 20.3 | | | 20 | 190 | 380 | 2.4 | 99.37 | 2.0 |
| | | 1503 | 0 | | 20.3 | | | 20 | 190 | | | | |

TABLE I

MMH WET SCRUBBER TEST DATA

Scrubber Bed Height - 7 ft.

Scrubber Liquor - Sodium Hypochlorite Solution

| Run No. | Date 1976 | Time | Scrubber Bed | | Liquor Flow Rate gpm | Liquor Strentgh % Avail. Chlorine | Storage Tank Temp. °F | $GN_2$ Flow Rate scfm | Temp. of MMH Vaporizes °F | Wet Chemistry Analysis | | | Drager Tube Analysis of Outlet Gas, ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | ΔP, in. of water | Temp. °F | | | | | | Inlet Gas ppm | Outlet Gas ppm | Absorb. Effec./, Percent | |
| 5. | 8-18 | 1310 | 2.3 | 106 | 19.1 | 5.09 | 104 | 430 | 182 | 200 | 25 | 87.5 | 0 |
| | | 1317 | 2.3 | 106 | 19.7 | | 104 | 430 | 182 | 310 | 8.6 | 97.23 | 0 |
| | | 1325 | 2.3 | 106 | 19.7 | | 104 | 430 | 192 | 700 | 15 | 97.86 | 0 |
| 6. | 8-18 | 1403 | 0 | 96 | 20.2 | | 104 | 20 | 188 | 250 | 5 | 98.00 | 0 |
| 7. | 8-18 | 1518 | 0 | --- | 20.9 | 3.0 | --- | 20 | 184 | 10,000 | 4.5 | 99.96 | 0 |
| | | 1528 | 0 | --- | 20.9 | | --- | 20 | 184 | 950 | 2.5 | 99.74 | 0 |
| 8. | 8-19 | 0945 | 0 | 106 | 20.1 | | 106 | 20 | 183 | 330 | 1.7 | 99.48 | 0 |
| | | 1015 | 0 | 106 | 20.1 | | 106 | 20 | 181 | 1360 | 1.0 | 99.93 | 0 |
| | | 1045 | 0 | 106 | 20.1 | | 106 | 20 | 181 | 600 | 1.0 | 99.83 | 0 |
| 9. | 8-19 | 1210 | 0 | 114 | 20.0 | | 116 | 100 | 177 | 830 | 7.5 | 99.10 | 0 |
| | | 1240 | 0 | 114 | 20.0 | | 116 | 100 | 178 | 1380 | 7.5 | 99.46 | 0 |
| | | 1310 | 0 | 120 | 20.2 | | 124 | 100 | 179 | 315 | 8.4 | 98.92 | 0 |
| 10. | 8-19 | 1355 | 0 | 120 | 20.2 | | 124 | 200 | 180 | 940 | 9.5 | 98.99 | 0.25 |
| | | 1425 | 0 | 126 | 20.2 | 0.71 | 130 | 200 | 182 | 282 | 7.2 | 98.12 | 0.25 |
| | | 1455 | 0 | 126 | 20.2 | | 130 | 200 | 182 | 45 | 1.0 | 97.78 | 0 |

## TABLE II

## $N_2O_4$ WET SCRUBBER TEST DATA

Scrubber Bed Height - 4 ft.

Scrubber Liquor - Sodium Hydroxide Solution

| Run No. | Date 1976 | Time | Scrubber Bed | | Liquor Flow Rate gpm | Liquor Strength Percent NaOH | $GN_2$ Flow Rate scfm | Temp. of MMH Vaporizer °F | Wet Chemistry Analysis | | | Drager Tube Analysis of Output Gas, ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Δ P, in. of water | Temp. °F | | | | | Inlet Gas, ppm | Outlet Gas, ppm | Absorb. Effec., Percent | |
| 1. | 8-26 | 1125 | --- | 97 | 20.8 | 7.52 | 100 | 97 | 637 | 232 | 63.57 | |
| 2. | 8-26 | 1140 | 0.1 | 97 | 20.8 | | 20 | 97 | 862 | 202 | 76.56 | 200 |
| | | 1200 | 0.1 | 97 | 20.8 | | 20 | 96 | 1750 | 200 | 88.60 | 250 |
| | | 1230 | 0.1 | 97 | 20.8 | | 20 | 94 | 2670 | 226 | 01.2 | |
| | | 1250 | 0.1 | 97 | 20.8 | 5.96 | 20 | 94 | 5000 | 253 | 94.9 | |
| | | 1305 | 0.1 | 97 | 20.8 | 4.88 | 20 | 91 | 3330 | 232 | 93.1 | |

TABLE II

$N_2O_4$ WET SCRUBBER TEST DATA

Scrubber Bed Height - 7 ft.

Scrubber Liquor - Sodium Hydroxide Solution

| Run No. | Date 1976 | Time | Scrubber Bed | | Liquor Flow Rate gpm | Liquor Strength Percent NaOH | $GN_2$ Flow Rate scfm | Temp. of $N_2O_4$ Vaporizer °F | Wet Chemistry Analysis | | | Olfactron Detector Analysis of Output Gas, ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Δ p, in. of water | Temp. °F | | | | | Inlet Gas, ppm | Outlet Gas, ppm | Absorb. Effec., Percent | |
| 3. | 8-26 | 1440 | 0.3 | 97 | 20.6 | 4.60 | 20 | 93.5 | 4990 | 152 | 96.93 | |
| | | 1500 | 0.3 | 97 | 20.6 | | 20 | 93.5 | 4890 | 155 | 96.83 | |
| 4. | 8-26 | 1530 | 0.3 | 97 | 20.6 | 4.08 | 50 | 93.5 | 3600 | 166 | 95.39 | |
| 5. | 8-27 | 0815 | 0.2 | -- | 20.4 | 4.16 | 50 | 95 | 1250 | 150 | 88.00 | |
| | | 0820 | 0.2 | 90 | 20.4 | | 50 | 93 | 3625 | 167 | 95.39 | |
| | | 0900 | 0.2 | 90 | 20.3 | | 50 | 88 | 3125 | 185 | 94.01 | |
| | | 0942 | | 90 | 20.3 | 3.77 | 50 | 105 | 3950 | 193 | 95.12 | |
| | | 0950 | | 90 | 20.4 | | 50 | 102 | 4180 | 102 | 97.56 | 115 |
| 6. | 8-27 | 1015 | 0.7 | 90 | 20.5 | | 100 | 100 | 3450 | 244 | 92.93 | 360 |
| | | 1033 | 0.7 | 90 | 20.5 | | 100 | 103 | 2470 | 104 | 95.79 | 360 |
| | | 1048 | 0.7 | 90 | 20.5 | 3.54 | 100 | | 2400 | 94 | 96.08 | 360 |
| | | 1108 | 0.7 | 90 | 20.5 | | 100 | 105 | 3320 | 168 | 94.91 | 360 |
| | | 1125 | 0.7 | 90 | 20.5 | | 100 | 103 | 2400 | 218 | 90.92 | 300 |
| | | 1146 | 0.7 | 90 | 20.5 | | 100 | 106 | 1120 | 280 | 75 | 320 |
| 7. | 8-27 | 1339 | 0.5 | 92 | 20.5 | | 100 | 94 | 1260 | 161 | 87.22 | 120 |
| | | 1348 | 0.5 | | 20.5 | 3.13 | 100 | 94.2 | 1200 | 200 | 85.42 | 150 |
| | | 1407 | | | 20.5 | | 100 | 94.2 | 1310 | 214 | 83.7 | 150 |
| | | 1430 | | | 20.5 | | 100 | 93.3 | 2710 | 265 | 90.72 | 250 |
| | | 1445 | 0.3 | 96 | 20.5 | 2.96 | 100 | 92.2 | 3000 | 224 | 92.53 | 250 |

TABLE II (cont)

$N_2O_4$ WET SCRUBBER TEST DATA

Scrubber Bed Height - 7 ft.

Scrubber Liquor - Sodium Hydroxide Solution

| Run No. | Date | Time 1976 | Scrubber Bed | | Liquor Flow Rate gpm | Liquor Strength, Percent NaOH | $GN_2$ Flow Rate scfm | Temp. of $N_2O_4$ Vaporizer °F | Wet Chemistry Analysis | | | Olfactron Detector Analysis of Output Gas, ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | ΔP, in. of water | Temp. °F | | | | | Inlet Gas, ppm | Outlet Gas, ppm | Absorb. Effec., Percent | |
| 7. | (cont) | 1459 | | | 20.5 | | 100 | 91.0 | 2730 | 290 | 89.39 | 290 |
| | | 1514 | 0.3 | | 20.5 | | 100 | 97.0 | 3300 | 292 | 91.16 | 310 |
| | | 1529 | 0.3 | | 20.5 | 2.67 | 100 | 99.5 | 3300 | 282 | 91.59 | 360 |
| 8. | 8-30 | 1053 | 0.8 | | 20.4 | 2.48 | 200 | 108 | 803 | 218 | 72.85 | |
| | | 1106 | 0.6 | | 20.4 | | 200 | 107.5 | 788 | 159 | 79.82 | |
| | | 1120 | 0.6 | | 20.4 | | 200 | 107 | 788 | 166 | 78.93 | |
| | | 1135 | 0.8 | | 20.4 | | 200 | 106 | 1900 | 278 | 85.37 | |
| | | 1150 | 0.8 | | 20.4 | | 200 | 103 | 1925 | 282 | 85.35 | |
| | | 1205 | 0.8 | | 20.4 | | 200 | 104.5 | 1850 | 282 | 84.76 | |
| | | 1220 | 0.8 | | 20.4 | | 200 | 103.5 | 1900 | 225 | 88.16 | |
| | | 1235 | 0.8 | | 20.4 | 2.10 | 200 | 107 | 2000 | 390 | 80.50 | |
| | | 1250 | 0.8 | 81 | 20.4 | | 200 | 104 | 1650 | 345 | 79.09 | |
| | 1316 | 1316 | 0.8 | 81 | 20.4 | | 200 | 104 | 1800 | 315 | 82.5 | |
| | | 1333 | 0.8 | 81 | 20.4 | | 200 | 112 | 1800 | 760 | 57.77 | |
| | | 1348 | 0.8 | 81 | 20.4 | 1.76 | 200 | 117 | 1680 | 760 | 54.76 | |
| 9. | 8-30 | 1355 | | 81 | 20.4 | | 50 | 116 | 2530 | 276 | 89.09 | |
| 10. | 8-30 | 1415 | 0.3 | 81 | 20.4 | | 20 | 116.5 | 5800 | 315 | 94.56 | |
| 11. | 8-30 | 1452 | 0.3 | | 20.4 | | 20 | 108 | 13,800 | 170 | 98.77 | |
| | | 1501 | 0.3 | | 20.4 | | 20 | 118 | 14,650 | 144 | 99.22 | |
| | | 1509 | 0.3 | | 20.4 | | 20 | 116 | 18,000 | | | |

TABLE II (cont).

## $N_2O_4$ WET SCRUBBER TEST DATA

Scrubber Bed Height - 7 ft.

Scrubber Liquor - Sodium Hydroxide Solution

| Run No. | Date 1976 | Time | Scrubber Bed | | Liquor Flow Rate, gpm | Liquor Strength Percent NaOH | $GN_2$ Flow Rate scfm | Temp. of $N_2O_4$ Vaporizer °F | Wet Chemistry Analysis | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | ΔP, in of water | Temp. °F | | | | | Inlet Gas, ppm | Outlet Gas, ppm | Absorb. Effec., Percent |
| 12. | 8-30 | 1522 | 0.1 | | 20.4 | | 10 | 112 | 9250 | 108 | 98.83 |
| | | 1546 | 0.1 | | 20.4 | | 10 | 112 | 14,000 | 68 | 99.51 |
| | | 1603 | 0.1 | | 20.4 | | 10 | 116 | 14,650 | 151 | 98.96 |
| 13. | 8-30 | 1615 | 0.6 | | 20.4 | .48 | 200 | 111 | 300 | 88.5 | 70.5 |
| 14. | 8-30 | 1712 | 0.8 | | 20.4 | 1.4 | 200 | 110 | 52.5 | 32 | 39.0 |
| 15. | 8-30 | 1734 | | | 20.4 | | 20 | | 410,000 | 900 | 99.78 |
| | | 1738 | | | 20.4 | | 20 | | 27,250 | 84 | 99.69 |
| | | 1744 | | | 20.4 | 1.22 | 20 | | 20,000 | 80 | 99.6 |

TABLE III

FLOW AND TEMPERATURE CONDITIONS FOR OFF-GAS SAMPLING

Date: 8-17-76

| Time | Flow Reading | Flow Rate Ml/Min. | Gas Temp °C | Remarks |
|---|---|---|---|---|
| 9:20 | 54 | 1010 | 25 | |
| 9:25 | 53 | 1000 | 26 | |
| 9:30 | 54 | 1010 | 25 | |
| 10:00 | 56 | 1040 | 26 | |
| 10:15 | 52 | 980 | 26 | Adjusted flow |
| 11:00 | 55 | 1025 | 29 | |
| 11:15 | 53 | 1000 | 29 | |
| 11:30 | 54 | 1010 | 29 | |
| 11:45 | 54 | 1010 | 30 | |
| 12:00 | 52 | 980 | 32 | Adjusted flow |
| 12:45 | 56 | 1040 | 33 | |
| 1:00 | 54 | 1010 | 37 | |
| 1:15 | 53 | 1000 | 36 | |
| 1:30 | 56 | 1040 | 35 | |
| 1:45 | 54 | 1010 | 34 | |
| 2:30 | 54 | 1010 | 39 | |
| 2:45 | 54 | 1010 | 34 | |
| 3:00 | 52 | 980 | 33 | Adjusted flow |
| 3:10 | 53 | 1000 | 32 | End test reading |
| Date: 8-18-76 | | | | |
| 1:10 | 49 | 900 | 31 | |
| 1:15 | 50 | 930 | 30 | |
| 1:30 | 51 | 970 | 31 | |
| 1:45 | 54 | 1010 | 29 | |
| 1:55 | | | | Adjusted MMH flow<br>Reduced NaOCl from 5 to 3% |
| 2:45 | 50 | 930 | 25 | |
| 3:10 | 50 | 930 | 29 | |
| 3:25 | 50 | 930 | 23 | Smoke from stack |
| 3:30 | 45 | 810 | 26 | Shut Down |

TABLE III (cont.)

Date: 8-19-76

| Time | Flow Reading | Flow Rate Ml/Min. | Gas Temp °C | Remarks |
|---|---|---|---|---|
| 12:00 | 50 | 930 | 27 | |
| 12:15 | 50 | 930 | 29 | |
| 12:30 | 54 | 1010 | 28 | |
| 1:00 | 60 | 1170 | 30 | Adjusted flow to 54 |
| 1:30 | 55 | 1025 | 30 | |
| 1:45 | 50 | 930 | 33 | Adjusted flow to 54 |
| 2:00 | 55 | 1025 | 33 | |
| 2:30 | 60 | 1170 | 36 | Adjusted flow to 54 |
| 3:00 | 50 | 930 | 37 | |

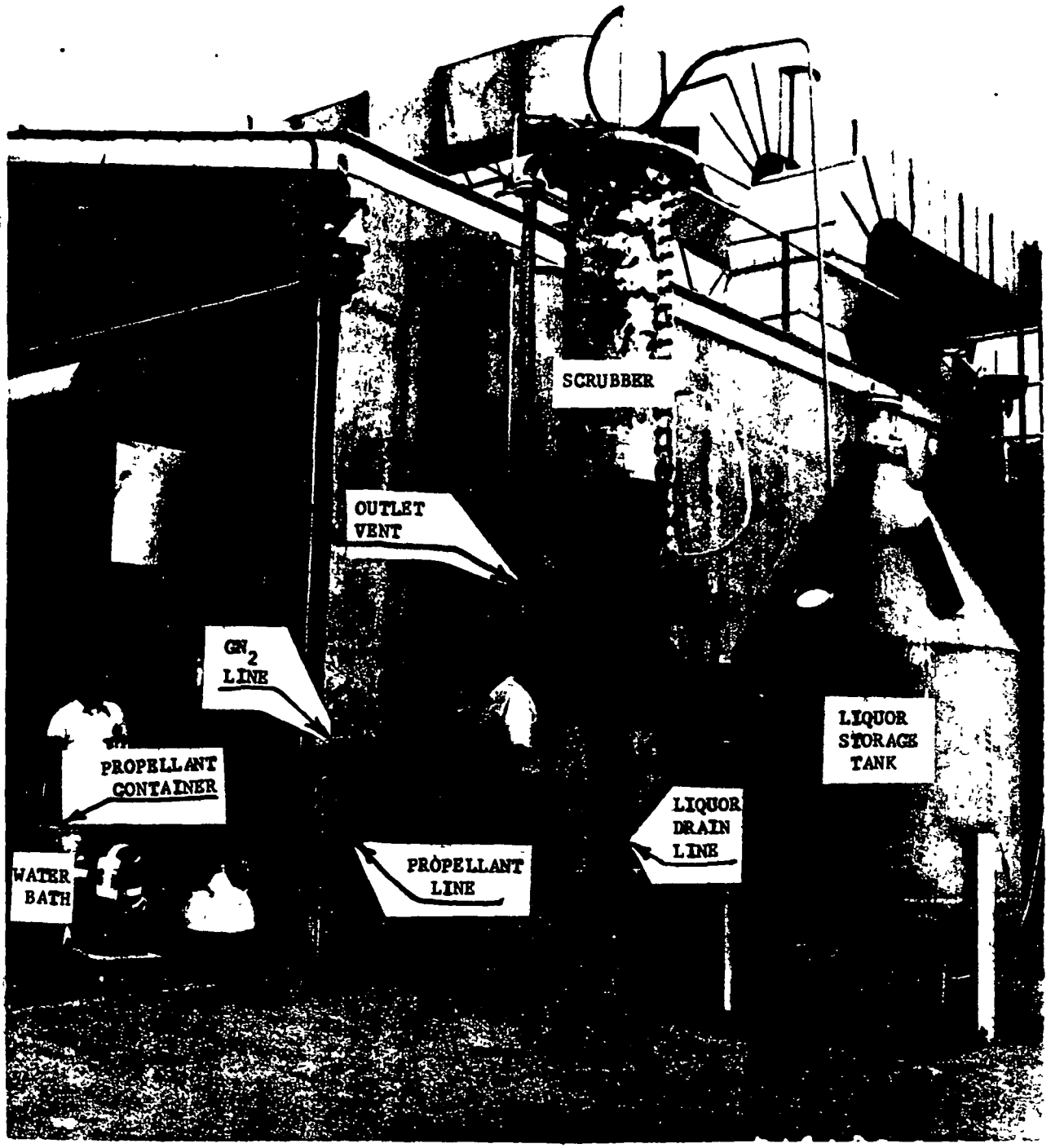


FIGURE 1 - WET SCRUBBER TEST SET-UP

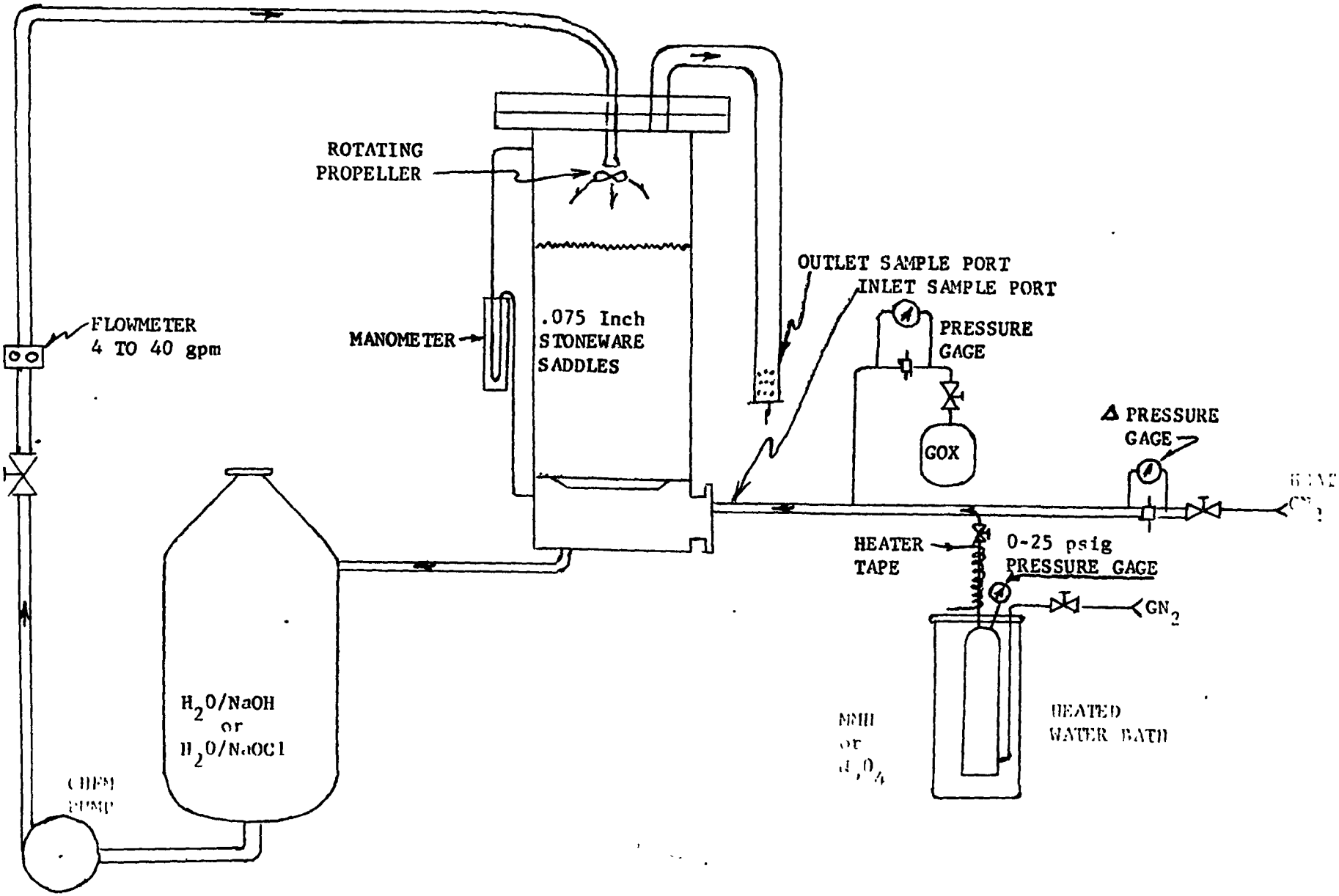


FIGURE 2. WET SCRUBBER SCHEMATIC

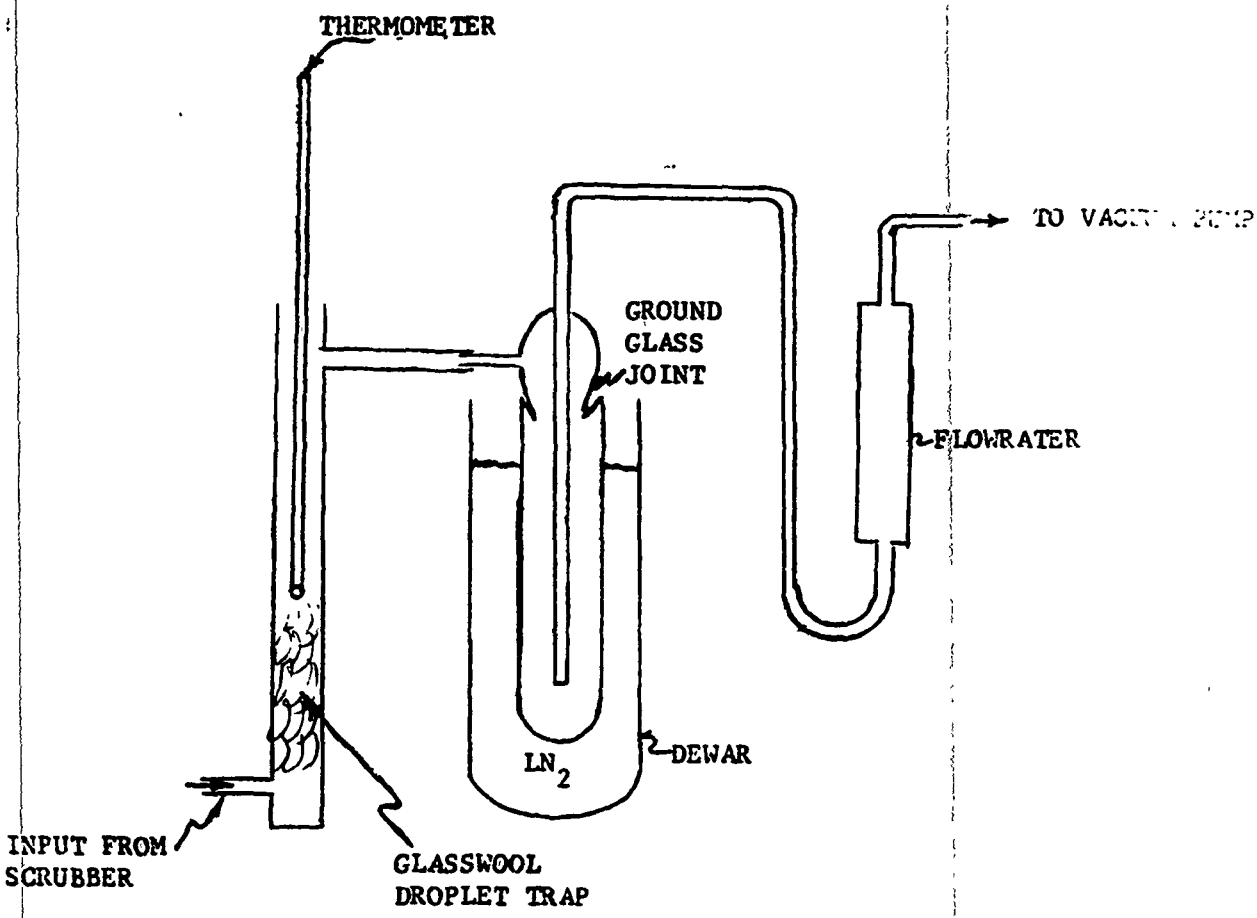


FIGURE #3 - OFF GAS SAMPLING SET-UP

# STANDARD TITLE PAGE

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15. Supplementary Notes

This report covers Task 2 Phase VI of VI.

16. Abstract

This report covers experiments with wet (water) scrubbing concepts for removing Monomethyl Hydrazine (MMH) and Nitrogen Tetroxide ($N_2O_4$)vapors from vent gas (Nitrogen or Helium) streams. The data includes a large scale prototype test.

| 17 KeyWords | 18 Distribution Statement |
|---|---|
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